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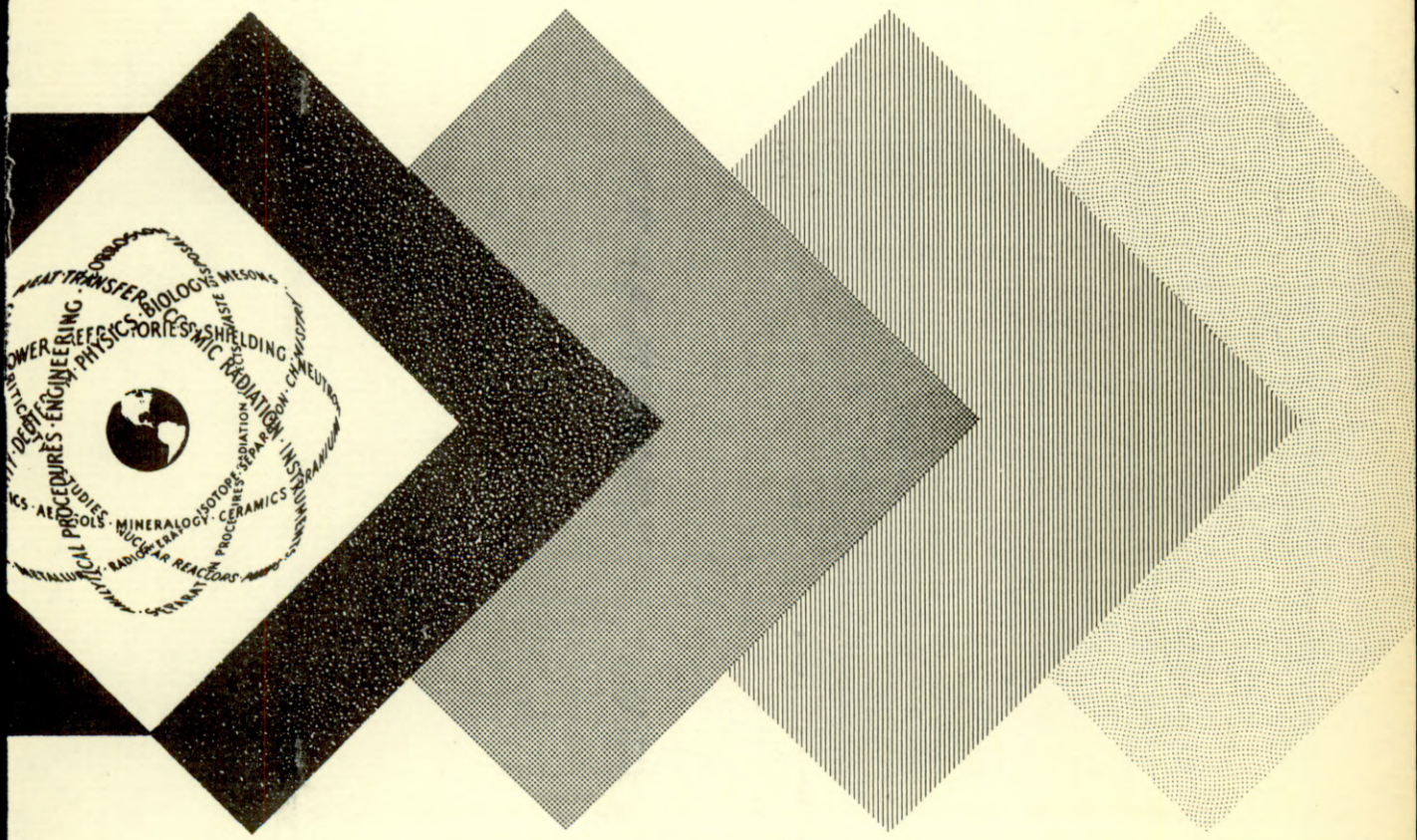
THE CHEMISTRY, PURIFICATION AND METALLURGY OF PLUTONIUM

Edited by
Charles Allen Thomas

December 1944

Metallurgical Laboratory
Chicago University
Chicago, ~~Ohio~~ Illinois



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THE CHEMISTRY, PURIFICATION AND METALLURGY OF PLUTONIUM

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Book 1

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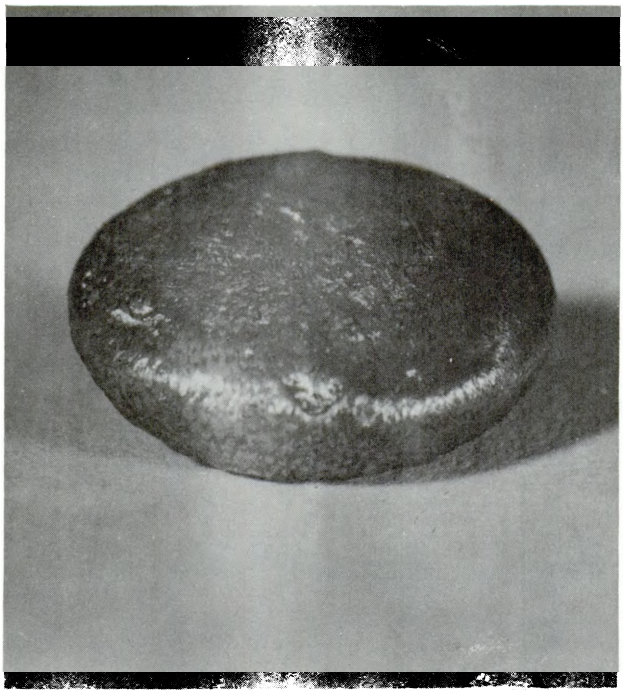

A ten gram regulus of pure plutonium
as it comes from the reduction bomb.
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PREFACE

The material presented in this Monograph came from research work which had for its principal object the preparation of plutonium in a very high state of purity. In the latter part of July, 1944, the extreme high purity specifications of plutonium were removed and this aspect of the program was accordingly modified. At this time there was such encouraging progress in our research that I have every reason to believe that the objective of obtaining plutonium in the specified high state of purity could have been achieved completely and on time.

At the close of the program we were given a directive to compile a final report covering the work done on the chemistry, purification and metallurgy of plutonium so that the work could be resumed with a minimum loss of time. We hope that this volume will make it possible for any skilled chemists or metallurgists not only to acquire a first-hand knowledge of the work but also to take up the program and complete it satisfactorily.

I am indebted to the two Project Directors, Dr. A. H. Compton and Dr. J. Robert Oppenheimer, for the splendid cooperation they have afforded me in the coordination and direction of this work. They have made important contributions to its progress.

I particularly wish to thank Dr. F. W. H. Zachariasen who is responsible for Chapter IV, "The Crystal Chemistry of Plutonium and Its Compounds", and Colonel Stafford L. Warren for Chapter XII, "Health Hazards in the Handling of Plutonium".

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To the Manhattan District, United States Engineer Office, we are indebted for important assistance in providing the facilities for carrying on this work. The Area Engineers at the various locations of the Project were at all times most helpful.

I wish to thank the editorial staff for its cooperation in preparing the individual sections of the Monograph. The compiling and rewriting of the original manuscripts was largely the work of Dr. J. C. Warner. To him go my sincere thanks for bringing the Monograph to final completion.

Finally, my congratulations are extended to the scientists whose names appear as participants in this work. The mass of accurate scientific information in this Monograph is a clear indication of the notable progress that may be expected when a group of scientists are afforded the opportunity of working in close cooperation and with all the implements of modern scientific methods at their disposal.

Charles Allen Thomas,
Final Purification and Metallurgical Director.

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CHAPTER I

INTRODUCTION

This monograph on the physical and chemical properties of plutonium is the culmination of an intensive and productive research effort by American scientists working under the stress of a national emergency. Consequently, the monograph is distinguished in many respects from the bulk of our chemical literature.

In the first place, this monograph represents the first compilation of the physical and chemical properties of a synthetic radioactive element. It gives an account of extensive investigations of its fundamental chemistry, purification and metallurgy. Anyone reading this account will be convinced that plutonium, in spite of its expected similarity to its neighbors in the Periodic System, is endowed with a set of characteristic chemical and physical properties which make it one of the most interesting of the elements.

Another interesting aspect of this monograph is that it so clearly illustrates the accelerating pace of scientific research and development in this decade. Less than four years have elapsed since plutonium was first synthesized by the bombardment of uranium with deuterons in the cyclotron at Berkeley, California. In the brief time that has passed since this discovery, its properties have been extensively studied as the content of this monograph reveals. Certainly plutonium is no longer the least familiar element in the Periodic Table. This rapid accumulation of

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knowledge is in startling contrast to the slow development of our knowledge of radioactivity following the pioneer discovery of Becquerel.

Finally, this monograph is added evidence of the skill and energy with which American scientists have met the present national emergency. There are many tributes to the genius and initiative of American scientists and technicians working under the stress of war, but none of these achievements is more noteworthy than the excursion into new and unexplored fields of knowledge which is represented here.

Element 94 was discovered late in 1940 by Seaborg, McMillan, Wahl and Kennedy, in uranium bombarded with deuterons in the Berkeley 60-inch cyclotron. The isotope discovered was later shown to be 94^{238}. Early in 1941 the isotope of major interest, 94^{239}, was discovered by Seaborg, Segrè, Kennedy and Lawrence, in uranium bombarded with neutrons formed in the Berkeley cyclotron. More recently, another isotope of plutonium, 94^{240}, has been recognized. This isotope is formed by the absorption of neutrons by 94^{239}. Element 94 was given the name plutonium, symbol Pu, to follow uranium and the previously discovered neptunium in the same order as the corresponding planets.

Investigation of the chemical and physical properties of plutonium has been in progress continuously since the element's discovery. During the first year and a half, researches were done with isotope Pu^{238}, using the tracer technique. Indeed, this isotope is more suitable for research on a tracer scale than Pu^{239} because its much shorter half-life permits approximately a thousand-fold greater sensitivity in its detection by alpha particle emission. The first pure plutonium in the form

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of compounds of the isotope Pu^{239} was isolated in August of 1942 in experiments on the ultra-micro scale with amounts of Pu^{239} ranging from 1 to 200 micrograms.

These experiments, on the so-called "microgram scale", differed in principle from the experiments on the tracer scale in that the work was done with pure plutonium compounds at the usual concentrations used in the investigation of the chemical properties of an element. This was accomplished in spite of the extraordinarily small amounts of material available by working with extremely small volumes, usually of the order of 10^{-3} ml., with the help of specially constructed small capillary containers, burettes, and so forth, together with extremely sensitive ultra-micro balances and specially adapted microscopes. In this manner the more stable oxidation states, (IV) and (VI), were established and the solubilities of many of the important compounds of plutonium were measured. The presently accepted exact value for the half-life of Pu^{239} was determined to be 24,300 years, and this formed the basis for one of the best methods of assaying for this isotope. Metallic plutonium was produced, the methods for production of metallic plutonium were studied in some detail, and preliminary estimates of physical properties such as the density and the melting point were made. It was even possible to establish the exact formulas of a number of important compounds by X-ray diffraction experiments using such small amounts. These experiments extended over a period of about a year and a half, and the total amount of plutonium in the laboratory at any time during this period never exceeded a few hundred micrograms.

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Work continued on approximately this scale of operation until about January of 1944, at which time milligram amounts of Pu^{239} became available. Since then, the investigations have continued with larger amounts of material; experiments on a gram scale becoming possible in March, and on a ten gram scale in July, 1944. Experimental work using "stand-ins" for plutonium (i.e., other more abundant elements such as uranium, thorium or cerium which have certain chemical or physical properties similar to plutonium) also contributed much to these investigations. Almost invariably the techniques later used in experiments with plutonium were explored first by the use of stand-ins.

It is interesting to note that chemical plants costing many millions of dollars were designed and put under construction on a basis of the results of experiments with only micrograms of plutonium; this is indeed a unique accomplishment, even in America.

This survey is thus based upon work which was started with tracer scale experiments and has since been confirmed and extended by experiments with larger amounts of material. The major portion of the information which is being reported has been confirmed by experiments with these larger amounts of plutonium.

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NUCLEAR-PHYSICAL PROPERTIES OF PLUTONIUM

Isotopes.— Two of the three known isotopes of plutonium, Pu^{238} and Pu^{239}, are formed by the bombardment of U^{238}. Using deuterons as the bombarding projectiles in the cyclotron and very high energies, a d,2n (deuteron in, 2 neutrons out) reaction is induced which leads to the formation of Pu^{238}. At this energy and at lower energies of bombardment there occur also the d,n reaction (deuteron in, neutron out) and the d,p reaction (deuteron in, proton out), both of which lead to the formation of Pu^{239}. This isotope, Pu^{239}, may also be formed by direct neutron bombardment of uranium, using slow neutrons, to give essentially the same chain as is obtained in the d,p reaction mentioned above. This reaction may be carried out in the cyclotron for producing small amounts of Pu^{239} for tracer work. For the production of larger amounts of material, a "pile" is utilized. Equations for these nuclear reactions leading to Pu^{238} and Pu^{239} are listed below.

(1) $92^{U^{238}}$ (d,2n) $93^{Np^{238}}$ $\xrightarrow[2.0\ d]{\beta^-}$ $94^{Pu^{238}}$ $\xrightarrow[\sim 50\ y]{\alpha}$

(2) $92^{U^{238}}$ (d,n) $93^{Np^{239}}$ $\xrightarrow[2.33\ d]{\beta^-}$ $94^{Pu^{239}}$ $\xrightarrow[24{,}300\ y]{\alpha}$

(3) $92^{U^{238}}$ (d,p) $92^{U^{239}}$ $\xrightarrow[23\ m]{\beta^-}$ $93^{Np^{239}}$ $\xrightarrow[2.33\ d]{\beta^-}$ $94^{Pu^{239}}$ $\xrightarrow[24{,}300\ y]{\alpha}$

(4) $92^{U^{238}}$ (n,γ) $92^{U^{239}}$ $\xrightarrow[23\ m]{\beta^-}$ $93^{Np^{239}}$ $\xrightarrow[2.33\ d]{\beta^-}$ $94^{Pu^{239}}$ $\xrightarrow[24{,}300\ y]{\alpha}$

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A third isotope of plutonium, Pu^{240}, is formed by the absorption of neutrons by Pu^{239}. The cross section for this reaction is rather large, amounting for thermal neutrons to nearly one-half the cross section for the fission of Pu^{239}. This results in the formation of an appreciable percentage of this isotope mixed with Pu^{239} in the present methods for the production of Pu^{239}.

Fission.-- One of the most interesting nuclear-physical properties of plutonium is that of fission. Upon interacting with a slow neutron, most readily with one having thermal energy only, the Pu^{239} nucleus is ruptured with the release of two or three energetic neutrons, an occasional alpha particle, energetic gamma radiation, and the formation of two atomic nuclei of lower atomic number which have the residual mass of the plutonium atom divided unequally between them. This is essentially the same process of fission which other heavy nuclei such as the uranium nucleus of mass number 235 are known to undergo. The slow neutron fission cross section of Pu^{239} is of the same order of magnitude as that of U^{235}. This property of Pu^{239} makes it a source material for atomic (nuclear) power.

The isotope Pu^{240}, unlike Pu^{239}, undergoes spontaneous fission at a relatively high rate corresponding to a "half-life" for the process of some 10^{11} years (compare to a half-life for spontaneous fission of Pu^{239} of approximately 10^{16} years). This means that a mixture of Pu^{239} and Pu^{240} must contain less than 0.005 per cent of Pu^{240} in order to keep the neutron emission below about 3 neutrons per minute per gram.

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Radiations.— The alpha particle given off by Pu^{238} has an energy of 5.5 Mev and a mean range of about 4.1 cms. in air at 15°C. and 760 mm. pressure. The alpha particle from Pu^{239} has an energy of 5.15 Mev and a mean range in air of about 3.68 cms.

It has been found that even the most highly purified Pu^{239} seems to carry with it an inseparable spectrum of soft quantized radiation. Lead absorption curves indicate the presence of a gamma ray of about 0.4 Mev energy, one of 0.065 Mev, and two or more softer rays. The absorption and energy data are given in Table I-1. The abundance figure for the 0.4 Mev gamma ray may be off by a factor of two. The reliability of the other abundance figures is even less certain. The doubtfulness is due to the lack of reliable information on the counting efficiencies (fraction of quanta traversing the G-M tube that register counts) for the several rays. The 0.4 Mev gamma efficiency is the value of one per cent per Mev (i.e., 0.4 per cent) while the efficiency one per cent was arbitrarily chosen for the softer rays.

Table I-1. Properties of Radiations from Plutonium

Half thickness (g/cm^2)	Mass absorp. coefficient $1\ g^{-1}\ cm^{-1}$	Wave length (Å)	Abundance (per α particle)	Energy (Mev)
1.5 (Pb)	---	---	10^{-4}	0.4
1.90 (Al)	0.365	0.243	2×10^{-4}	0.065
0.141 (Al)	4.91	0.694	.017	0.018
0.0453 (Al)	15.3	1.02	.02	0.012
0.005 (Al)*	---	---	---	---

* Probably soft conversion electrons.

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These gamma rays and X-rays might come about as the result of a branching in the alpha emission from the Pu^{239}. The data are consistent with the view that (1) about one in 10,000 of the alphas have an energy 0.4 Mev lower than the 5.15 Mev of the normal alpha particle, and thus leave the product U^{235} nucleus in an excited state, which is then restored to its ground state by the emission of 0.4 Mev gamma rays; (2) about one in 50 of the alphas have an energy 0.065 Mev lower than the normal, resulting in the emission of 0.065 Mev gamma rays, approximately 99 per cent of which undergo conversion in the L-shell, with the formation of soft electrons and X-rays of 0.012 and 0.018 Mev.

Half-Life of Pu^{239}.-- The half-life of Pu^{239} has been determined as 24,300 years, with a probable error of about one per cent. This value was obtained by measuring the rate of alpha emission of specially prepared and weighed samples of a pure plutonium compound. Pure PuO_2 was weighed and dissolved in acid, and accurately measured aliquots of the solution were evaporated on platinum plates for alpha particle measurements. These were made both in low-geometry counters, for which the geometry factor can be accurately calculated, and in the standard parallel-plate ion chambers which are known to have a "counting yield" of 52 per cent (greater than 50 per cent, the geometry factor, because of backscattering of alpha particles by the platinum mounts). The specific activity so obtained is 136,500 disintegrations per minute per microgram, or 71,000 counts per minute per microgram on platinum in a parallel-plate counter.

The half-life may be measured in another way -- by comparison of

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the rate of beta particle disintegration of one of the parent materials (U^{239} or Np^{239}) of known half-life, with the rate of alpha particle disintegration of the product Pu^{239} after complete decay of the parent. This method was used before weighable amounts of pure plutonium were available. The direct comparison with Np^{239} is complicated by the presence of a large proportion of conversion electrons in its spectrum so that the comparison with U^{239} was necessary. Two determinations gave 2.0×10^4 years and 2.5×10^4 years, respectively, the average being close to the more precise figure obtained by the weighing-measuring experiments.

The isotope Pu^{240} must surely emit alpha particles, but the half-life for this process and the energy of the alpha particles have not yet been determined.

THE PURIFICATION PROBLEM

When nuclei of most of the elements of low atomic number (approximately ≤ 20) are bombarded with alpha particles of energies comparable to those emitted by plutonium, neutrons are emitted with yields in the range of 6.6×10^{-5} to 10^{-8} neutrons per alpha particle. For one of the preferred methods of application of the isotope Pu^{239}, there are nuclear-physical reasons for desiring metallic plutonium which will not emit more than three neutrons per minute per gram. Inasmuch as most neutrons from Pu^{239} result from the bombardment of the nuclei of light element impurities by plutonium alphas, it became necessary to undertake research to find methods for preparing metallic plutonium of extremely high purity.

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Tolerance Limits.-- To set the objectives for the purification program one needed to know the neutron per alpha ratio for each of the light elements so that tolerance limits for each element in plutonium could be set. These ratios were in general determined by bombarding a target of the light element with alphas from polonium as a stand-in for plutonium and then making a correction for the difference in the energies of Po and Pu alphas. These studies led to the table of tolerance limits given in Table I-2 for the various light elements in plutonium.

Aim of the Program.-- When one realizes that 1 ppm is only 0.0001 per cent and that any of these elements alone, present to the extent of the tolerance limit, would bring about an emission of three neutrons per minute per gram, the difficult character of the purification program can be appreciated. Since not one, but a number of light elements must be expected in product, it became the goal of those working on the chemical purification and metallurgy of plutonium to produce a metallic product in which the concentration of none of the light elements exceeded one-tenth of its tolerance limit. The entire problem consisted of two major subdivisions: (a) the conversion of the plutonium as it was received from the producing plants into a pure compound of plutonium suitable for reduction to metal, and (b) the reduction of the compound to metallic plutonium, remelting the metal and forming it into proper shapes without the introduction of undesirable impurities, and possibly achieving some purification during the remelting operation.

Special Analytical Methods.-- In support of the above purification and metallurgical program it was necessary to develop special analytical

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Table I-2.

Table of Tolerance Limits for Light Elements in Plutonium

Element	Limit in Pu, ppm
H	unlimited
He	unlimited
Li	1.3
Be	0.05
B	0.20
C	48
N	unlimited
O	77
F	1.7
Ne	5
Na	4.6
Mg	5.6
Al	11
Si	51
P	>350
S	3000
Cl	83
A	31
K	1000
Ca	4000

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methods capable of detecting the light element impurities in product at concentrations of the order of one-tenth the tolerance limits. The fact that until recently analyses had to be made on milligram samples of plutonium or its compounds placed unusually stringent requirements upon analytical methods. Even with larger amounts of product becoming available in recent months, its great value and the urgency of other experiments made the development of very sensitive methods for very small samples of product a matter of first rate importance.

For most of the light elements the analytical methods available when the purification program was begun were not sufficiently sensitive for the purpose; for some elements a satisfactory method was obtained by "scaling down" the known method, but for others it was necessary to develop entirely new methods.

At the time the purification program was terminated it was possible to analyze for the various light element impurities when present in the range of one-tenth of their tolerance limits, with a 610 mg. sample of plutonium. Of this amount, 460 milligrams were required in analyses for only three elements; namely, boron, fluorine and oxygen.

Prevention of Contamination.-- Early experiments on the micro- and milligram scale with stand-ins and with plutonium showed that one could easily contaminate product with some of the light elements in amounts equal to or in excess of their tolerance limits. The chief sources of this contamination were from dust in the laboratory air, from containers, and from reagent chemicals. This situation placed an additional burden on the final purification and metallurgy program, requiring the

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construction of "cleaned air" laboratories and the use of special containers and carefully purified chemicals. When chemicals of sufficient purity were not available from outside sources, it was necessary to purify the best available grades in the various Project laboratories.

ACHIEVEMENTS OF THE PROGRAM

The urgency of the purification program and the fact that research on the program was being done at a number of locations led, in May, 1943, to the appointment of a Final Purification and Metallurgical Director who was given the responsibility of coordinating and expediting the research on the program at all locations. Some of the locations were visited at regular intervals, but major emphasis was placed on monthly meetings held in Chicago and attended by the responsible directors of work on final purification and metallurgy in the various laboratories. These meetings served as a place for reporting research results, for the approval of research programs, and for the assignment of responsibilities on matters vital to the success of the purification program. After each meeting a formal report of the transactions was issued.

In the latter part of July, 1944, it was decided to place major emphasis on a final application method which did not require plutonium in a state of purity comparable to that which had been the aim of the program on final purification and metallurgy. As a consequence, the program, including the work on special analytical methods for light elements, has been abandoned and the responsibilities of the directors of the program are being brought to a close with the preparation of

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this monograph which will serve as a record of our achievements. How well we have succeeded can best be judged by reading Chapter II which shows that we already have been able to produce metallic plutonium of purity within the range of the tolerance limits for most of the light elements. We have every reason to believe that the objectives of the program could have been accomplished in full and in reasonable time.

It is not the object of this monograph to give an account of the work done by the various projects on the chemistry and technology of separations processes; however, the results of research on the fundamental chemistry of plutonium have been so important to the success of the program on purification and metallurgy that Chapter III is devoted to this subject.

Finally, it must be noted that no attempt is being made in this compilation to give specific credit to individuals for the research which is reported. The original and final research reports issued by the Ames, Berkeley, Chicago and Los Alamos Projects will fulfill this function. General credit is given in the Appendix by listing the names of the scientists who have participated in the purification and metallurgy program in the various laboratories.

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CHAPTER II

PRESENT PROCESS FOR THE PRODUCTION OF PURE PLUTONIUM

The first process for the purification and reduction of plutonium consisted of the following steps: (1) oxidation of the Pu(IV) nitrate to PuO_2^{++} by dichromate; (2) precipitation of $NaPuO_2Ac_3$; (3) solution of this precipitate in nitric acid and reprecipitation of $NaPuO_2Ac_3$; (4) solution of this precipitate in nitric acid and ether extraction of plutonyl nitrate; (5) a second ether extraction of the plutonyl nitrate after dissolving the first extract in water; (6) reduction to Pu(IV) with iodide and nitric acid; (7) evaporation to produce solid Pu(IV) nitrate or oxynitrate; (8) conversion to PuF_3, PuF_4 or $PuCl_3$ by treatment with HF or HCl, (9) reduction by lithium in a centrifuged bomb with a BeO liner. This procedure gave a product highly contaminated with light elements. A typical analysis has shown Li = 100 ppm, Be = 700 ppm, Na = 200 ppm, Mg = 60 ppm, Fe = 1000 ppm; these impurities would lead to a neutron emission of the order of 50,000 per gram per minute (to be compared with a desired level of 3 per gram-minute). This metal could be considerably improved by remelting. A typical sample after being twice remelted in tantalum contained Li = 25 ppm, Be = 50 ppm, Na = 15 ppm, Mg $<$ 5 ppm, Al = 100 ppm, K $<$ 20 ppm; the neutron emission calculated from this incomplete analysis is 3200 per gram-minute, and the neutron emission actually measured was 4400 per gram-minute.

Flowsheet for Purification and Metal Production.-- Gradually, the procedure outlined above was changed to the greatly improved scheme shown

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in the following flowsheet (Figure II-1). The chemical purification has been both simplified and improved by the inclusion of oxalate precipitations, the use of enclosed apparatus to minimize air-borne contamination and the elimination of unnecessary steps which increase contamination problems. Reductions are now carried out using either $PuCl_3$ or PuF_4 in MgO liners with pure calcium as the reducing agent. This improved reduction technique coupled with the old purification procedure and followed by remelting in cerium sulfide has produced metal which contained Li <1 ppm, Be <1 ppm, Na = 6 ppm, Mg = 7 ppm, Al = ~20 ppm, K <20 ppm, Fe = 150 ppm; this analysis is consistent with a neutron emission of 20 to 80 neutrons per gram-minute; the observed emission was 0 ± 100 per gram-minute.* The complete "best" procedure for producing plutonium free from light element impurities as shown in the flowsheet has never been properly tested because there has not existed simultaneously enough plutonium, adequate analytical methods (including neutron emission determination), complete quartz apparatus, and the need for plutonium free of light element impurities. However, experience with similar procedures and experience in the purification of elements used as stand-ins for plutonium (notably uranium and cerium) establish that the wet purification scheme outlined would probably meet all reasonable requirements associated with producing metal to meet the specifications of the tolerance table. Some problems still remained in obtaining sufficiently clean conditions in reduction and remelting, and the

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* The large uncertainty (± 100) was due to the small size of the sample. See Chapter XI for a discussion of neutron emission measurements.

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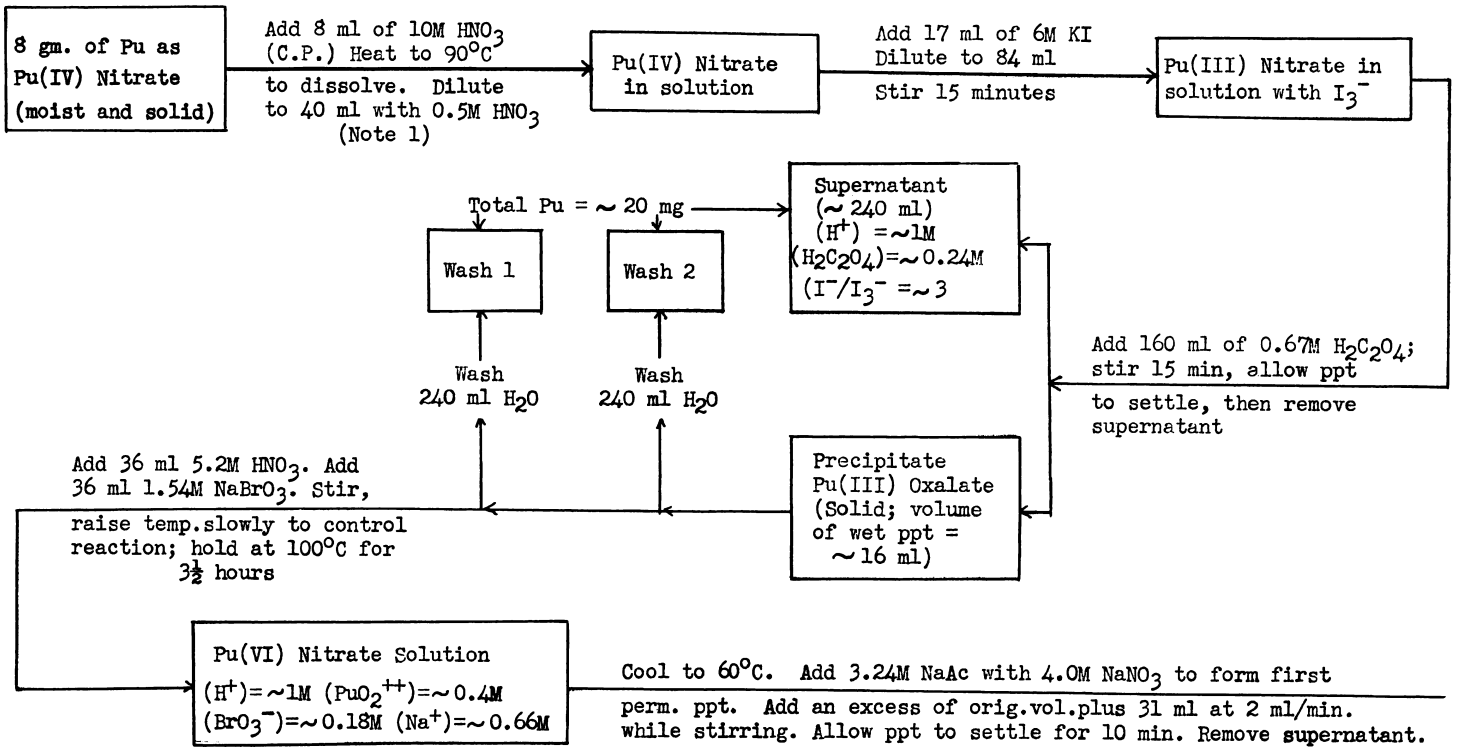
Fig. II-1.

Schematic Flowsheet for Production of Pure Plutonium (8 gram scale).


8 gm. of Pu as Pu(IV) Nitrate (moist and solid)
Add 8 ml of 10M HNO_3 (C.P.) Heat to 90°C to dissolve. Dilute to 40 ml with 0.5M HNO_3 (Note 1)
Pu(IV) Nitrate in solution
Add 17 ml of 6M KI Dilute to 84 ml Stir 15 minutes
Pu(III) Nitrate in solution with I_3^-
Total Pu = ~ 20 mg
Wash 1
Wash 2
Supernatant (~240 ml) (H^+) =~1M ($H_2C_2O_4$)=~0.24M (I^-/I_3^- =~3
Add 160 ml of 0.67M $H_2C_2O_4$; stir 15 min, allow ppt to settle, then remove supernatant
Wash 240 ml H_2O
Wash 240 ml H_2O
Precipitate Pu(III) Oxalate (Solid; volume of wet ppt = ~16 ml)
Add 36 ml 5.2M HNO_3. Add 36 ml 1.54M $NaBrO_3$. Stir, raise temp.slowly to control reaction; hold at 100°C for 3½ hours
Pu(VI) Nitrate Solution (H^+)=~1M (PuO_2^{++})=~0.4M (BrO_3^-)=~0.18M (Na^+)=~0.66M
Cool to 60°C. Add 3.24M NaAc with 4.0M $NaNO_3$ to form first perm. ppt. Add an excess of orig.vol.plus 31 ml at 2 ml/min. while stirring. Allow ppt to settle for 10 min. Remove supernatant.

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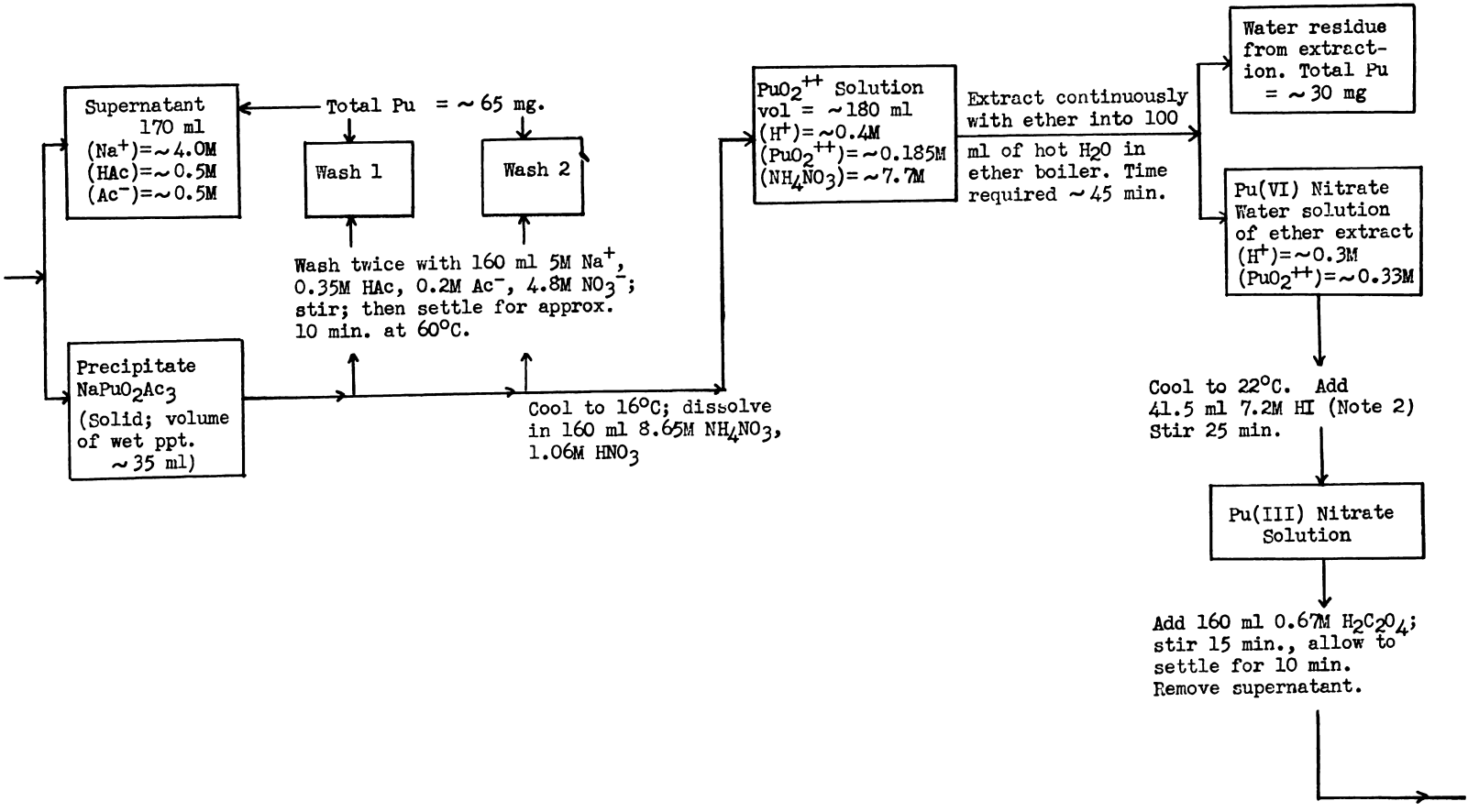
Supernatant
170 ml
$(Na^+)=\sim 4.0M$
$(HAc)=\sim 0.5M$
$(Ac^-)=\sim 0.5M$
Total Pu = ~ 65 mg.
Wash 1
Wash 2
Wash twice with 160 ml 5M Na^+, 0.35M HAc, 0.2M Ac^-, 4.8M NO_3^-; stir; then settle for approx. 10 min. at 60°C.
Precipitate
$NaPuO_2Ac_3$
(Solid; volume of wet ppt. ~ 35 ml)
Cool to 16°C; dissolve in 160 ml 8.65M NH_4NO_3, 1.06M HNO_3
PuO_2^{++} Solution
vol = ~ 180 ml
$(H^+)=\sim 0.4M$
$(PuO_2^{++})=\sim 0.185M$
$(NH_4NO_3)=\sim 7.7M$
Extract continuously with ether into 100 ml of hot H_2O in ether boiler. Time required ~ 45 min.
Water residue from extraction. Total Pu = ~ 30 mg
Pu(VI) Nitrate Water solution of ether extract
$(H^+)=\sim 0.3M$
$(PuO_2^{++})=\sim 0.33M$
Cool to 22°C. Add 41.5 ml 7.2M HI (Note 2) Stir 25 min.
Pu(III) Nitrate Solution
Add 160 ml 0.67M $H_2C_2O_4$; stir 15 min., allow to settle for 10 min. Remove supernatant.

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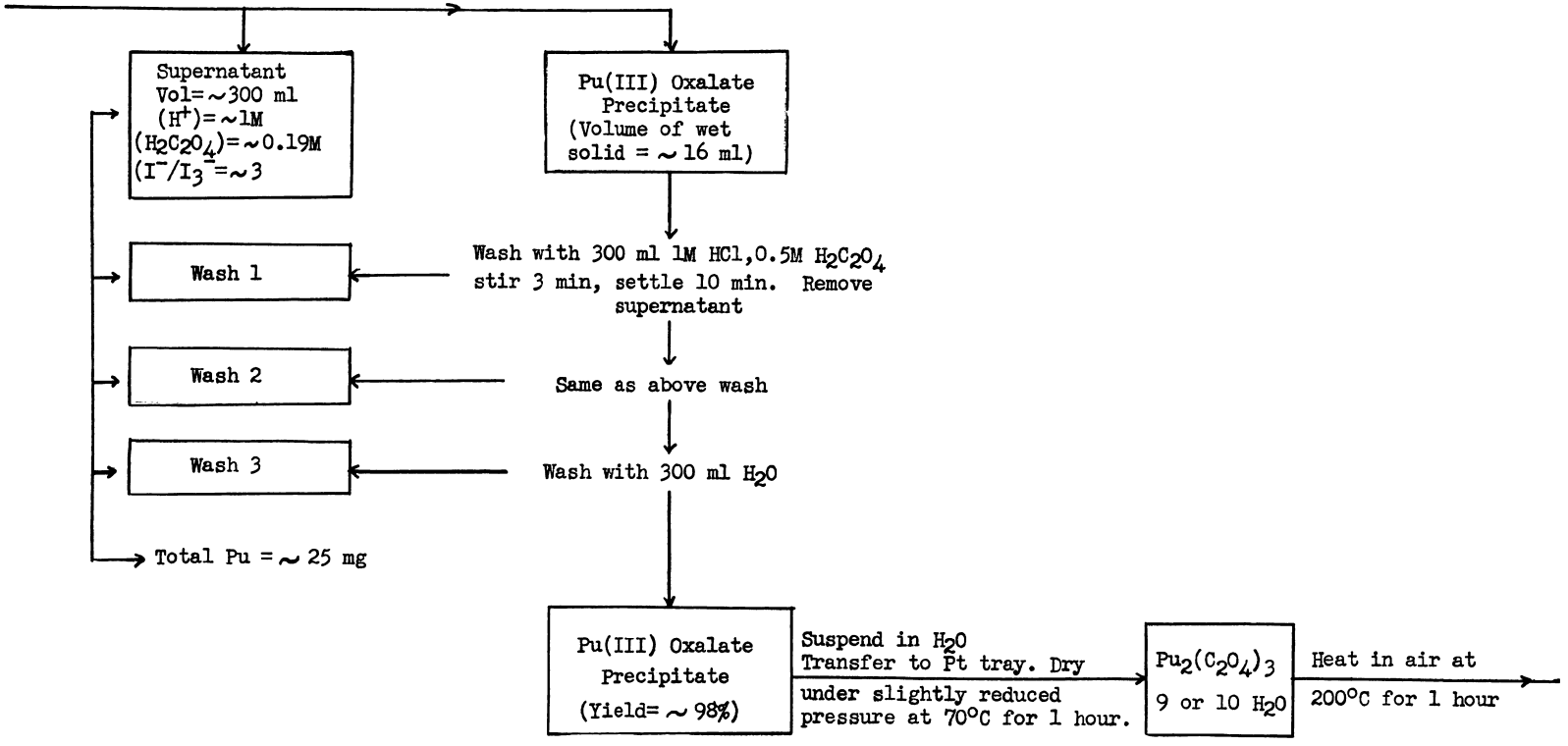
Supernatant
Vol=~300 ml
(H+)=~1M
(H2C2O4)=~0.19M
(I-/I3-=~3
Pu(III) Oxalate Precipitate (Volume of wet solid = ~ 16 ml)
Wash with 300 ml 1M HCl,0.5M H2C2O4 stir 3 min, settle 10 min. Remove supernatant
Wash 1
Same as above wash
Wash 2
Wash with 300 ml H2O
Wash 3
Total Pu = ~ 25 mg
Pu(III) Oxalate Precipitate (Yield= ~ 98%)
Suspend in H2O Transfer to Pt tray. Dry under slightly reduced pressure at 70°C for 1 hour.
Pu2(C2O4)3 9 or 10 H2O
Heat in air at 200°C for 1 hour

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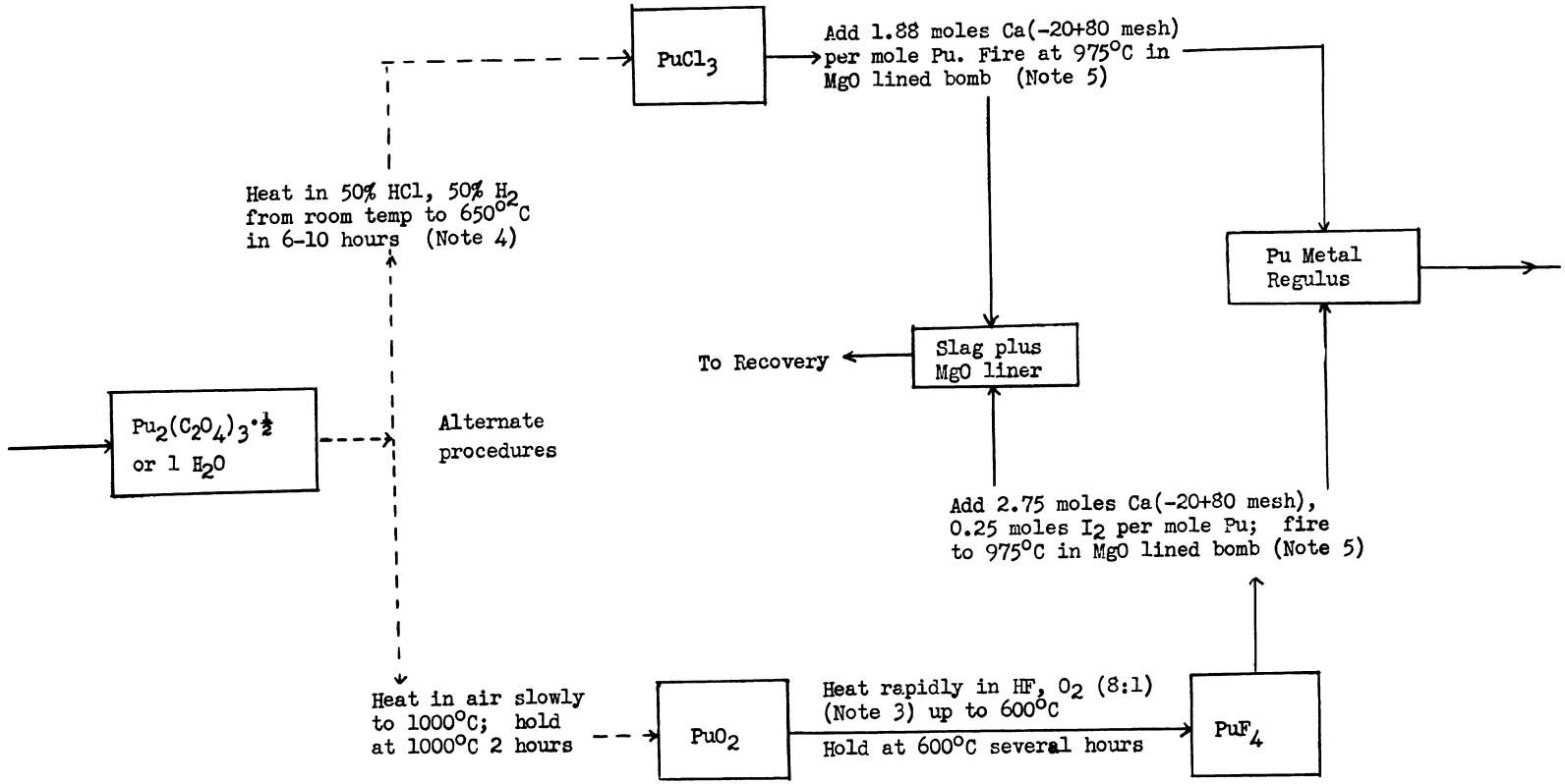
$PuCl_3$
Add 1.88 moles Ca(-20+80 mesh) per mole Pu. Fire at 975°C in MgO lined bomb (Note 5)
Heat in 50% HCl, 50% H_2 from room temp to 650°C in 6-10 hours (Note 4)
Pu Metal Regulus
To Recovery
Slag plus MgO liner
$Pu_2(C_2O_4)_3 \cdot \frac{1}{2}$ or 1 H_2O
Alternate procedures
Add 2.75 moles Ca(-20+80 mesh), 0.25 moles I_2 per mole Pu; fire to 975°C in MgO lined bomb (Note 5)
Heat in air slowly to 1000°C; hold at 1000°C 2 hours
PuO_2
Heat rapidly in HF, O_2 (8:1) (Note 3) up to 600°C
Hold at 600°C several hours
PuF_4

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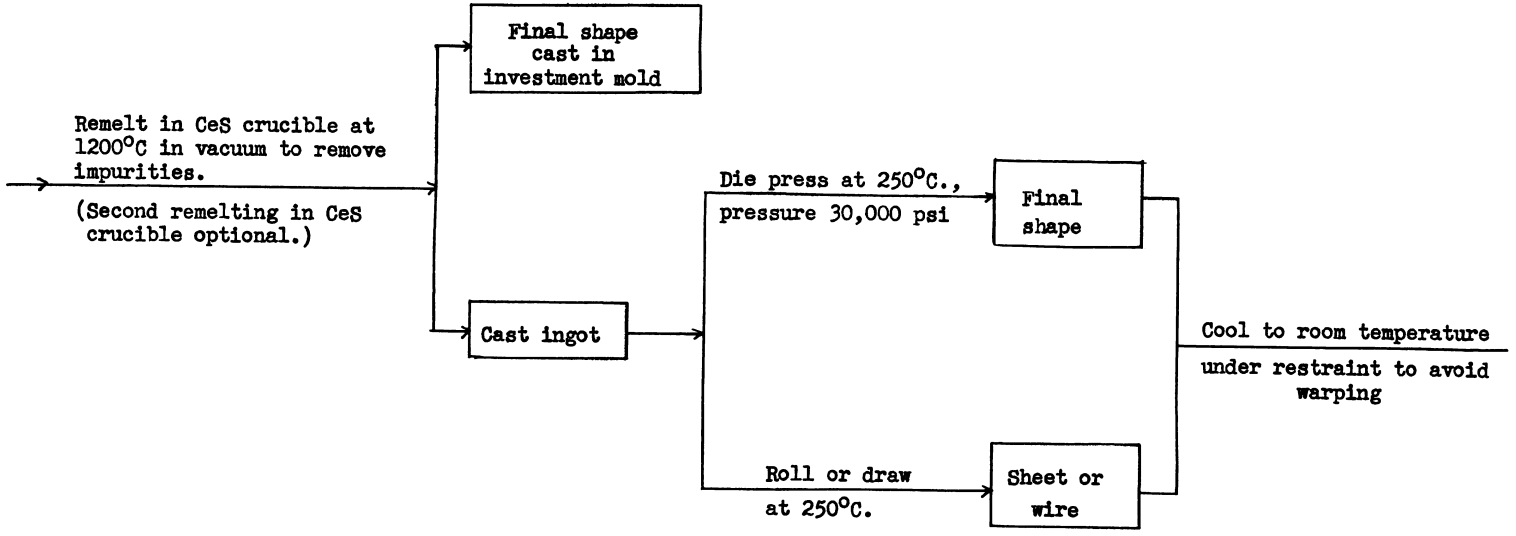
Final shape cast in investment mold
Remelt in CeS crucible at 1200°C in vacuum to remove impurities.
(Second remelting in CeS crucible optional.)
Die press at 250°C., pressure 30,000 psi
Final shape
Cast ingot
Cool to room temperature under restraint to avoid warping
Roll or draw at 250°C.
Sheet or wire

NOTES

1. If necessary, dilute somewhat further to dissolve.
2. Twice distilled, principally to remove phosphorus.
3. The rate of flow must be very rapid. On large scale it may be necessary to use this alternative procedure: Heat in HF, H_2 (1:1) to give PuF_3; heat this in HF, O_2 (8:1) to convert to PuF_4.
4. This might give C contamination. Believe this could be removed by treatment with Cl_2 and CO_2.
5. This temperature should probably be several hundred degrees lower on a 240 gm scale, and iodine content should be reduced.

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problem of oxygen impurity was not solved by the procedures of the flow-sheet.

Operations in Closed Systems.-- As described in detail in another chapter the handling of plutonium and its compounds presents very serious hazards to health as a result of its radioactive emission of alpha-particles. The various operations of the purification and reduction procedure must be performed with special precautions which are sometimes of such a nature as to restrict or modify the operations. In general, the dry operations are not particularly affected, since chemists are accustomed to the use of closed reaction trains, dry-boxes, etc. in such work. On the other hand, wet operations, especially those involving boiling or effervescence, are extremely dangerous if carried out in the customary way in any ordinary chemical fume hood. Also, the more or less open operations of wet chemistry expose highly purified materials to a serious amount of air-borne light element contamination. For these two reasons there has been developed an enclosed apparatus for the performance of all wet operations shown in the purification flowsheet. A photograph (Figure II-2) and a schematic diagram (Figure II-3) of this apparatus are included. This apparatus is constructed of Pyrex; an identical quartz apparatus should probably be used to produce the purest plutonium.

Scale of Operation.-- The apparatus pictured and the flowsheet included are for 8 gram batches; this is the present scale of operation. For full scale operation everything would be scaled up, probably to about 160 grams. This amount is safely below one-half of the critical mass in water and is a convenient multiple of the proposed 80-gram shipping container batch. Also, in the wet operations special precautions to avoid

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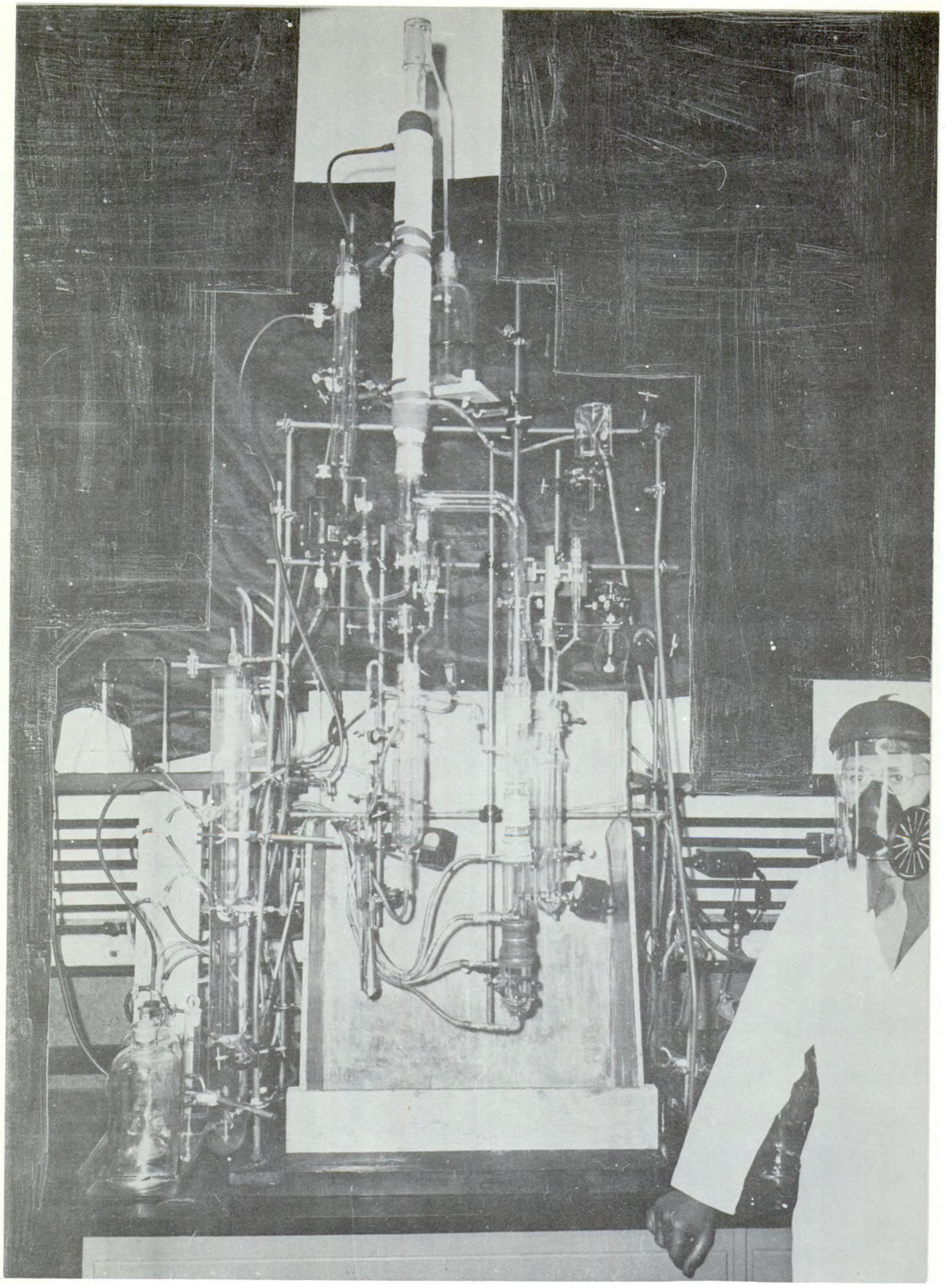

Fig. II-2.

Enclosed Apparatus for Wet Operations.

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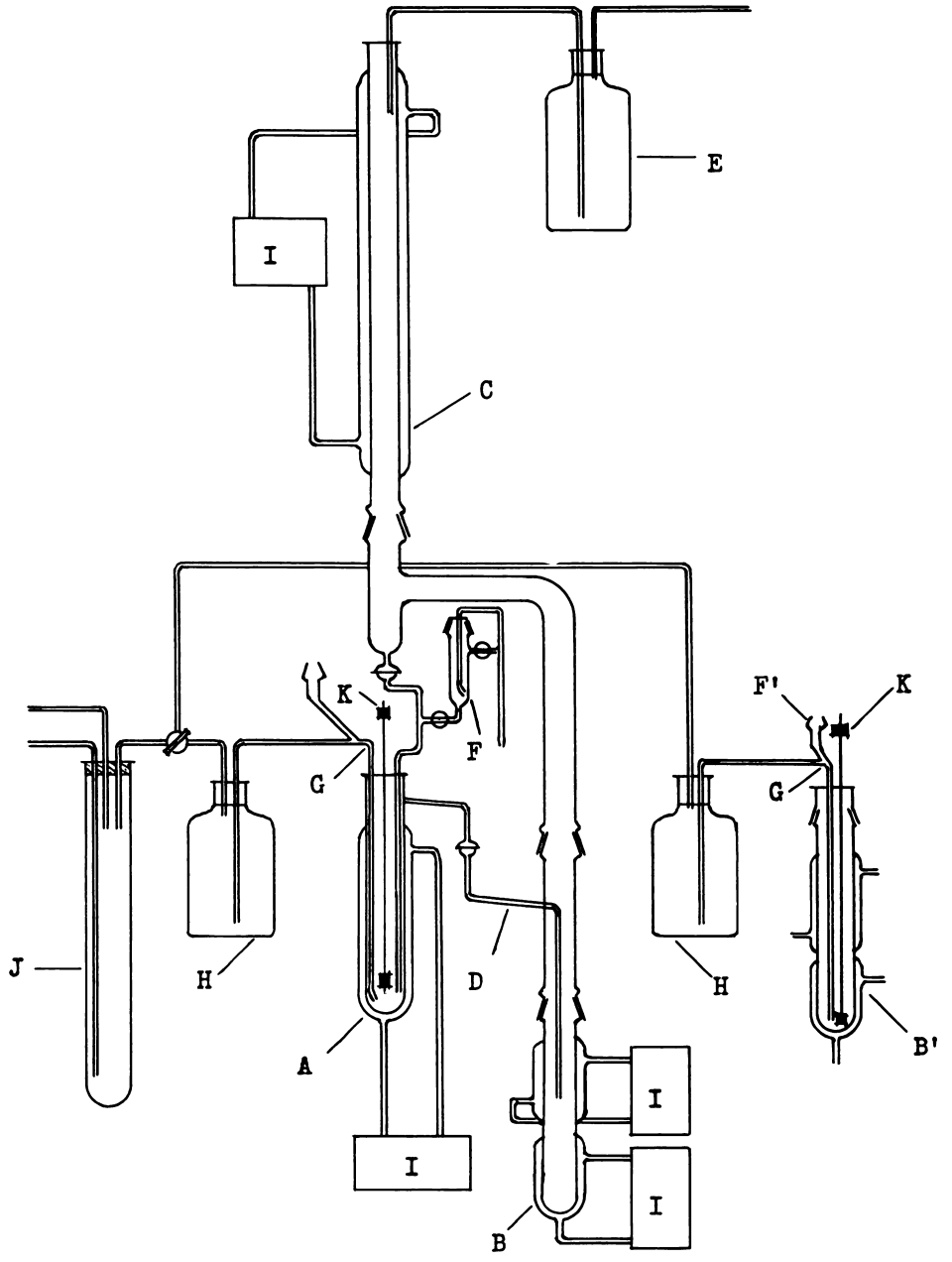

A - First precipitation and extraction tube
B - Second precipitation tube and ether boiler, in position for ether extraction
B'- B in position for second oxalate precipitation
C - Ether condenser
D - Loaded ether return
E - Ether storage
F - Product and reagent introduction tube
F'- Reagent introduction tube
G - Supernatant and wash solution withdrawal - 3 inch vertical motion
H - Supernatant and wash solution collection bottle
I - Heat exchanger and water circulating pump
J - Constant vacuum device
K - Motor driven stirrer

Fig. II-3. Diagram of Enclosed Apparatus for Wet Operations

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loss of plutonium in accidental breakage or spillage are desirable. A metal jacket with glass window, not shown in the photograph, is used to encase each reservoir of the apparatus that contains plutonium, and the entire apparatus may be placed in a splatter-proof box with a removable safety-glass front door. Also, in the event that plutonium from the production plant should be appreciably gamma-ray active (0.1 to 1 millicuries per gram) due to residual fission product contamination, this outer box and the metal jackets could be lined with lead to afford sufficient protection for the operators. After this purification step, the plutonium should be sufficiently purified so that its gamma-activity may be neglected in subsequent steps.

Conversion of Oxalate to Halide.-- The operations for converting the $Pu_2(C_2O_4)_3$ hydrate slurry to anhydrous PuF_4 or $PuCl_3$ are carried out in two enclosed trains. One train accomplishes the drying of the slurry, dehydration of the oxalate crystals and possibly the ignition to PuO_2 (if PuF_4 is desired); at present these manipulations are performed manually, but soon there will be in operation automatic trains in which platinum-rhodium boats containing the material are drawn by platinum-rhodium wires successively through regions of the proper temperature at the proper rate. A second train is used for treatment of the dry oxalate or oxide to convert it to $PuCl_3$ or PuF_4.

Reduction of Halide to Metal.-- The chloride or fluoride will be reduced to metal by reduction with calcium on a scale which it is eventually hoped will produce about 240 grams in each charge. The fluoride mixed with about 25 per cent excess calcium over the stoichiometric ratio and probably with additional calcium and iodine, is placed in a magnesium

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oxide liner contained in a steel bomb filled with argon and heated by high frequency induction to start the reaction. This method has been very reliable on a one to ten gram scale using either plutonium chloride or fluoride and has been thoroughly tested in semi-commercial operation on a 250 gram scale with uranium. Yields of at least 98 per cent -- probably 99 per cent -- are expected,* the unrecovered metal being partly in the calcium fluoride-calcium iodide slag, and to a lesser degree in the refractory liner. The choice between reducing $PuCl_3$ or PuF_4 should be made on the basis of whether or not the fluoride would lead to an undesirable amount of fluorine in the final metal.

Remelting and Forming Metal.-- The metal from the bomb reduction is in the form of a single clean biscuit easily freed from slag, but containing a small amount of calcium and magnesium in solution, and sometimes superficially adhering droplets of excess alkaline earth metal. The surface contamination can be removed by washing in water or dilute acetic acid or by electrolytic pickling. Though the calcium content in reduced metal is low, it is preferable to remove it by vacuum melting. This operation is not as yet thoroughly developed, but it is probable that it will be done in a cerium sulfide (CeS) crucible. The present practice is to carry the metal to a temperature of 1200°C. in a vacuum of 10^{-5} mm. mercury or better. From this point further treatment of the metal will depend in large measure upon the shapes needed. If roughly shaped buttons or simple, castable shapes are required, the metal will be solidified in the CeS crucible or will be cast directly in vacuum into a mold. Otherwise,

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* In a long run of 250 gram reductions of uranium, average yields of 99.6 per cent have been obtained by similar techniques.

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the buttons will be transferred to another vacuum melting furnace and cast by a bottom pouring arrangement into a suitable mold. This second casting operation does not involve high temperatures, as the metal casts satisfactorily at only 100°C. or so above the melting point. The use of a high grade MgO or possibly BeO refractory seems to be perfectly acceptable. If complex shapes are needed, molds made of silica, zircon or other investment molding materials are contemplated, while simple cylindrical or rectangular ingots will be cast in graphite or metal molds. The alpha form of Pu stable at room temperature is brittle; beta (stable between 115°C. and 225°C.) is malleable but moderately hard; gamma (existing between 225°C. and 310°C.) is very soft and plastic. Therefore, if fabrication is necessary into sheet, wire or small forgings, the necessary mechanical deformation will be done on the metal in the gamma state at a temperature of 225° to 325°C., which temperature is readily attained by an oil bath which provides both heat and suitable surface protection. Metallic surface coatings applied electrolytically or otherwise may minimize oxidation and the health hazard. There is no reason to doubt that gamma plutonium can be fabricated into any shapes that can be made with more conventional metals, for the working temperatures are low enough to permit the use of ordinary die steels. Designs to eliminate machining with its greath health hazard will be encouraged. To facilitate working of the material at ordinary temperatures, it is possible that plutonium will be alloyed so that the transformation at room temperatures from ductile beta or gamma to brittle alpha will be retarded or completely prevented. Final transformation to high density alpha by pressure, by prolonged heat treatment or cold treatment will be possible if the composition is properly chosen.

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CHAPTER III

FUNDAMENTAL CHEMISTRY OF PLUTONIUM

The need for a knowledge of the fundamental chemistry of plutonium in connection with the problems of purification and metallurgy resulted in an expansion and acceleration of the existing basic chemistry program and particular emphasis was placed on investigations of plutonium halides and oxides, as well as the metal itself. Early investigations were, of necessity, conducted on tracer and microgram scales since milligram and larger scale studies were only possible after February of 1944. These early investigations were extremely valuable since they provided a background of techniques as well as specific information which made it possible to perform larger scale experiments with considerable efficiency. As a result, the present knowledge of the fundamental chemistry of plutonium compares favorably in extent with that of uranium although it is incomplete in both cases.

In the last section of this chapter, an attempt is made to correlate the known chemical properties of plutonium with those of other elements in the Periodic Table and draw inferences as to its probable electronic structure. With the exception of this last section, fields of investigation corresponding, in general, to problems undertaken by various groups in cooperating laboratories have served as the basis for organizing the chapter.

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OXIDATION STATES

The Metallic State.-- At least four allotropic forms of Pu metal are known at the present time with transition temperatures in the vicinity of 115°, 225° and 310°C., the lowest being the only temperature adequately fixed. The low temperature (alpha) form has a density of about 19.8 gm. per cc. and an orthorhombic crystal structure similar to uranium. The beta form has a density of about 17.8 gm. per cc., and one of the higher temperature forms has a face-centered structure corresponding to a density of about 16.0 gm. per cc. The physical and chemical properties of metallic plutonium are discussed in detail in Chapter IX.

The metal is most readily prepared by thermal reduction of plutonium halides with strong reducing metals such as calcium. The similarity, in conditions employed, to the preparation of cerium metal by this same method is particularly marked. Electrolysis of fused halide baths is also feasible. Methods for the production of metallic plutonium are discussed in detail in Chapter VII.

The Monopositive and Dipositive States.-- No evidence has been obtained of the existence of Pu(I) or Pu(II) in aqueous solution. Two attempts were made to electrolytically reduce plutonium to an oxidation state lower than (III). A solution of Pu(III) in 1.0 M HCl was placed in the cathode compartment of a divided electrolytic cell and the solution was electrolyzed using a mercury cathode. The

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voltage was slowly raised to a maximum of 6 volts at which potential H_2 evolution was quite rapid. In a second similar experiment performed in 10 M HCl, the voltage was raised as high as 40 volts. No change in the appearance of the solution could be detected in either of these experiments, indicating that no reduction of plutonium had occurred. At the conclusion of the second experiment a portion of the Hg used as the cathode was removed, evaporated on a platinum foil and the foil counted for plutonium activity. A negligible amount of activity was found, indicating that reduction of Pu(III) to form an amalgam was insignificant in extent.

The compound PuO, discussed in the section on oxides in this chapter, is the best known compound of Pu(II) at present. This compound is readily soluble in dilute HCl with the liberation of H_2 which shows that Pu(II) is unstable in acid solution.

The Tripositive State.— Plutonium in the (III) oxidation state in aqueous solution has a characteristic blue color (violet under artificial light). The spectrum has several absorption bands which, in general, are narrow as is found with elements containing more than one f electron.* The absorption spectrum of Pu(III) in 0.5 N HCl is shown in Figure III-1.

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* The f electrons occur in deep lying sub-shells so that the electronic transitions are protected from the influence of the ion's environment, thereby giving rise to narrow absorption bands.

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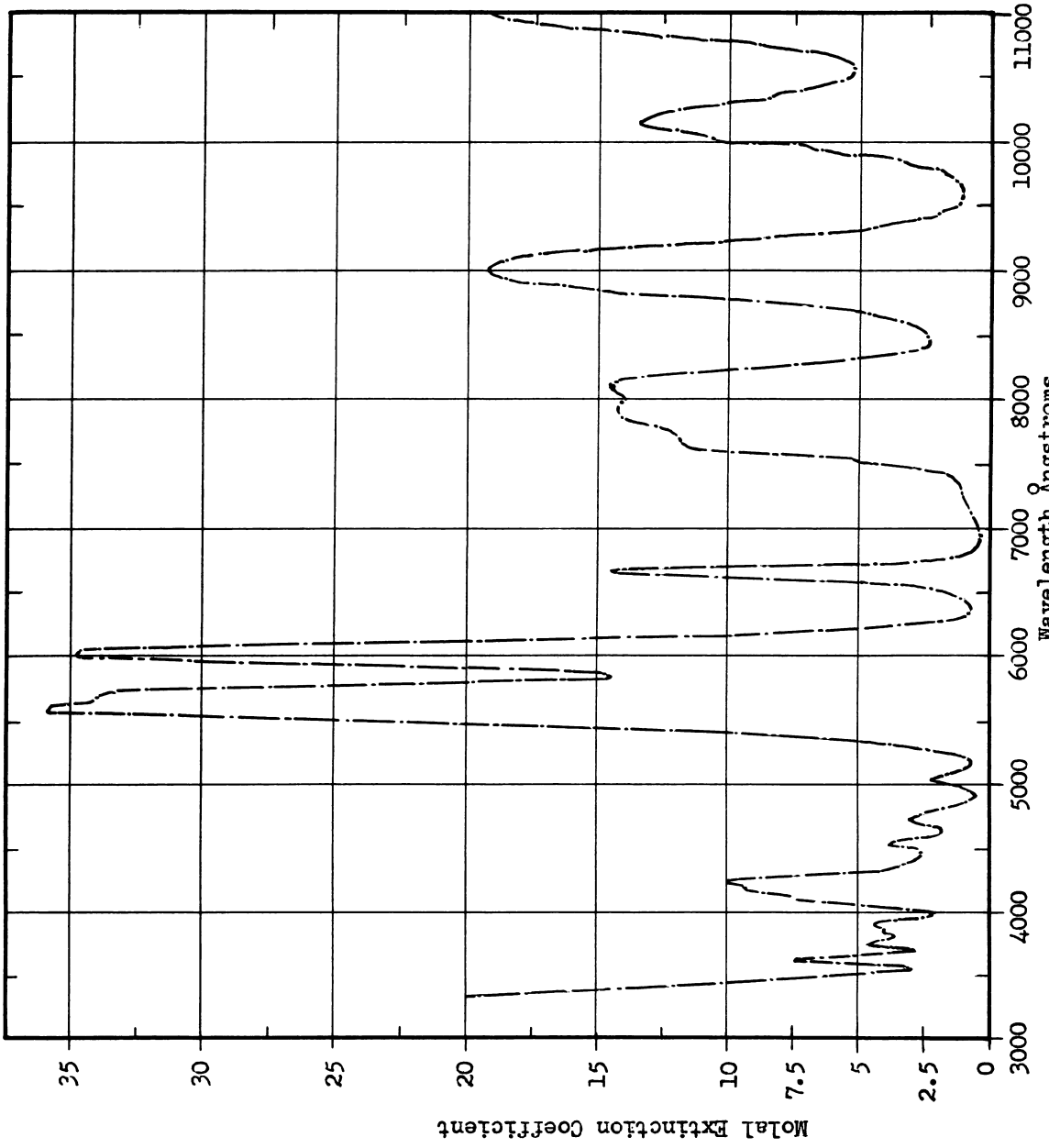

Fig. III-1. Absorption Spectrum of Pu(III) in 0.5 M HCl

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Because of its greater stability in aqueous solution, Pu(III) is of much more importance than the corresponding oxidation state of uranium. The general aqueous solution chemistry of Pu(III) seems to be very similar to that of the rare earth ions. This is probably due to a similarity in ionic radii and may indicate a similarity in electronic structure. Anhydrous halides and oxyhalides of Pu(III) may be readily prepared and are very similar to the rare earth trihalides and oxyhalides. In the trichloride and tribromide, Pu(III) has been shown to have an ionic radius almost identical with that of praesodymium.

Specific properties and compounds of Pu(III) are discussed in subsequent sections of this chapter.

The Tetrapositive State.— The color of aqueous solutions of Pu(IV) varies considerably. Concentrated solutions of Pu(IV) in strong HCl range in color from a light orange to nearly red, depending on the Pu(IV) concentration. In dilute HCl, dilute solutions of Pu(IV) are yellow-orange in color. In concentrated HNO_3 solution, Pu(IV) is green; in dilute HNO_3, Pu(IV) is green-yellow. These variations in color can be explained in part at least by the formation of various complex ions of Pu(IV) which are discussed later in this chapter. The absorption spectrum of Pu(IV) in 0.5 M HCl is shown in Figure III-2. It is evident that there are several sharp absorption bands as noted in the Pu(III) spectrum.

In aqueous solution, Pu(IV) is more stable than the corresponding

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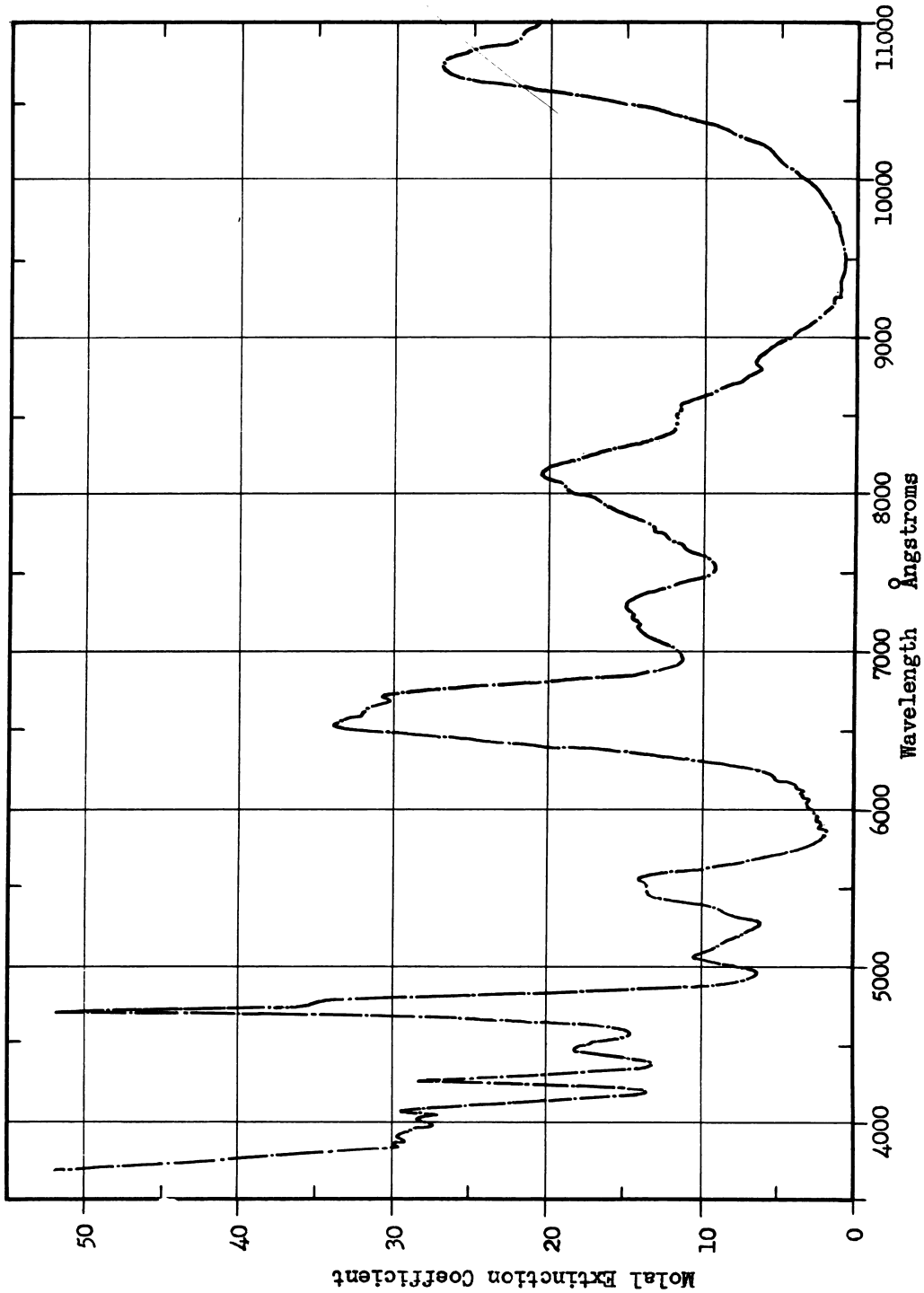

Fig. III-2. Absorption Spectrum of Pu(IV) in 0.5 M HCl

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oxidation state of uranium and closely resembles U(IV), Ce(IV) and Th(IV) in all its chemical properties except oxidation and reduction.

An important property of Pu(IV) is its extractability from aqueous solutions, containing high concentrations of nitrates, into various organic solvents. This property is discussed in detail in Chapter V. Other specific properties and compounds of Pu(IV) are discussed in subsequent sections of this chapter.

The Pentapositive State.-- As far as is known, no compounds of Pu(V) have been prepared.* Likewise, a pure aqueous solution of Pu(V), free of plutonium in other oxidation states, has not been prepared. However, it is known that the color intensity is much less than that of Pu(III), Pu(IV) or Pu(VI). Thus, on reducing Pu(VI) to Pu(V), the solution becomes nearly colorless. The absorption spectrum of Pu(V) has been measured only in solutions containing appreciable concentrations of Pu(III), Pu(IV) and Pu(VI). The curve given in Figure III-3 for pure Pu(V) in 0.5 M HCl was obtained by correcting the original absorption spectra data for the concentration of Pu(III), Pu(IV) and Pu(VI) present.

Little is known regarding the chemistry of Pu(V) other than its oxidation-reduction reactions which will be discussed later. Attempts

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* It has been suggested that the volatile higher fluoride of plutonium is the pentafluoride.

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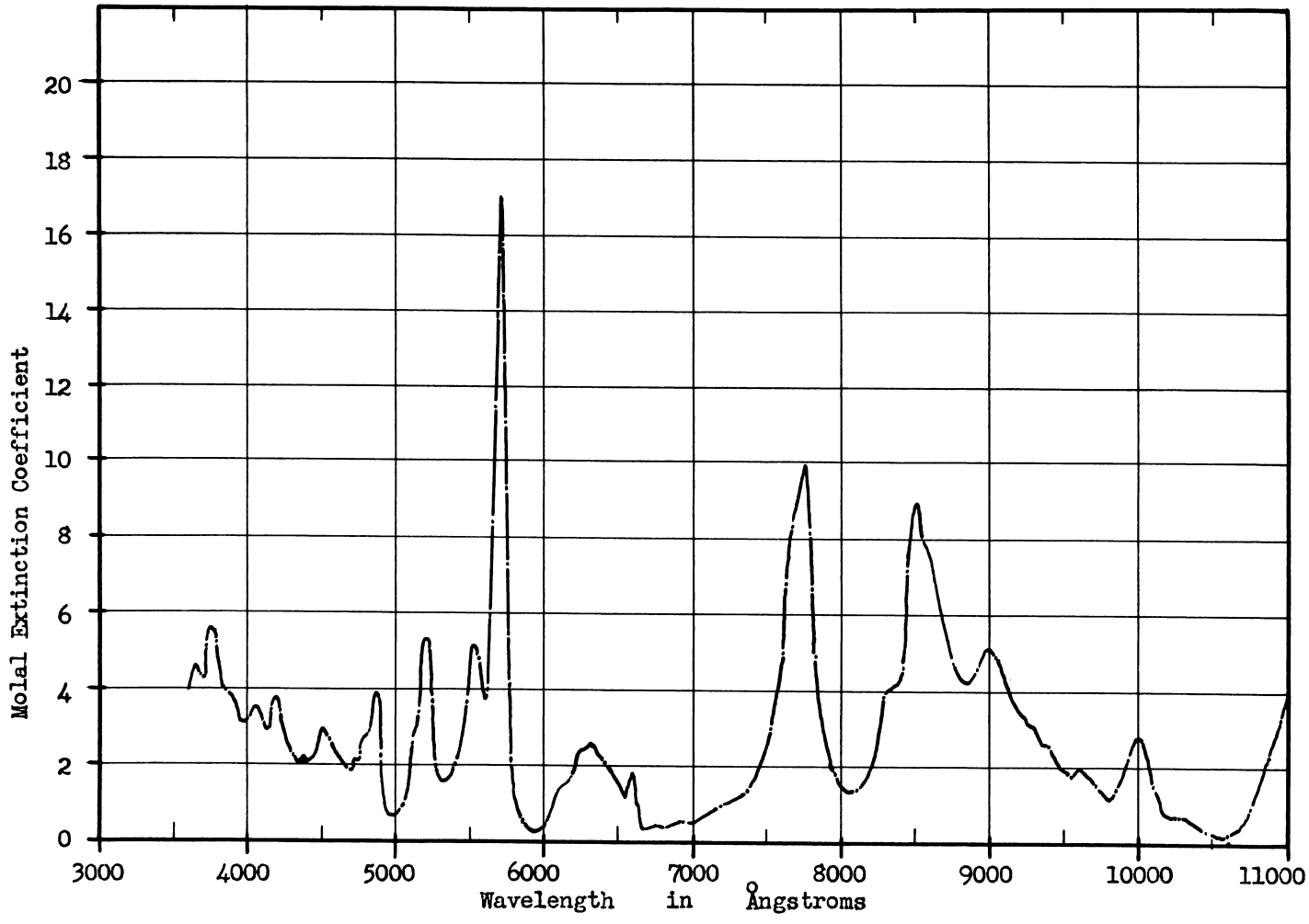

Fig. III-3. Absorption Spectrum of Pu(V) in 0.5 M HCl

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have been made to precipitate compounds of Pu(V), but without success. In several experiments excess hydroxide was added to Pu(V) solutions in order to precipitate the hydroxide, but in every case a brown or olive green precipitate was obtained which dissolved readily in acid to give a mixture of Pu(VI) and Pu(IV) and little, if any, Pu(V). The hydroxide precipitate is probably a mixture of Pu(IV) hydroxide and Pu(VI) hydroxide or plutonate. In other experiments no precipitate of Pu(V) was obtained with dilute acid solutions containing chloride ion, sulfate ion, or H_2O_2 at plutonium concentrations of one gram per liter.

Unlike the other oxidation states of plutonium, a close analogue of Pu(V) is not known at present.

The Hexapositive State.— Compounds and aqueous solutions of Pu(VI) range in color from pink through orange to brown. Plutonyl solutions, in general, appear orange with the actual color dependent upon the concentration. Plutonate solutions are brown. The absorption spectrum of Pu(VI) in 0.5 M HCl is shown in Figure III-4.

It is seen that the absorption bands are rather narrow, as with other oxidation states.

The chemistry of Pu(VI) closely follows that of U(VI) as far as is known. This is correlated with the fact that the ionic radius of Pu(VI) is only slightly smaller than that of U(VI). The two elements may have similar electronic structures.

The extraction of Pu(VI) from aqueous nitrate solutions into various

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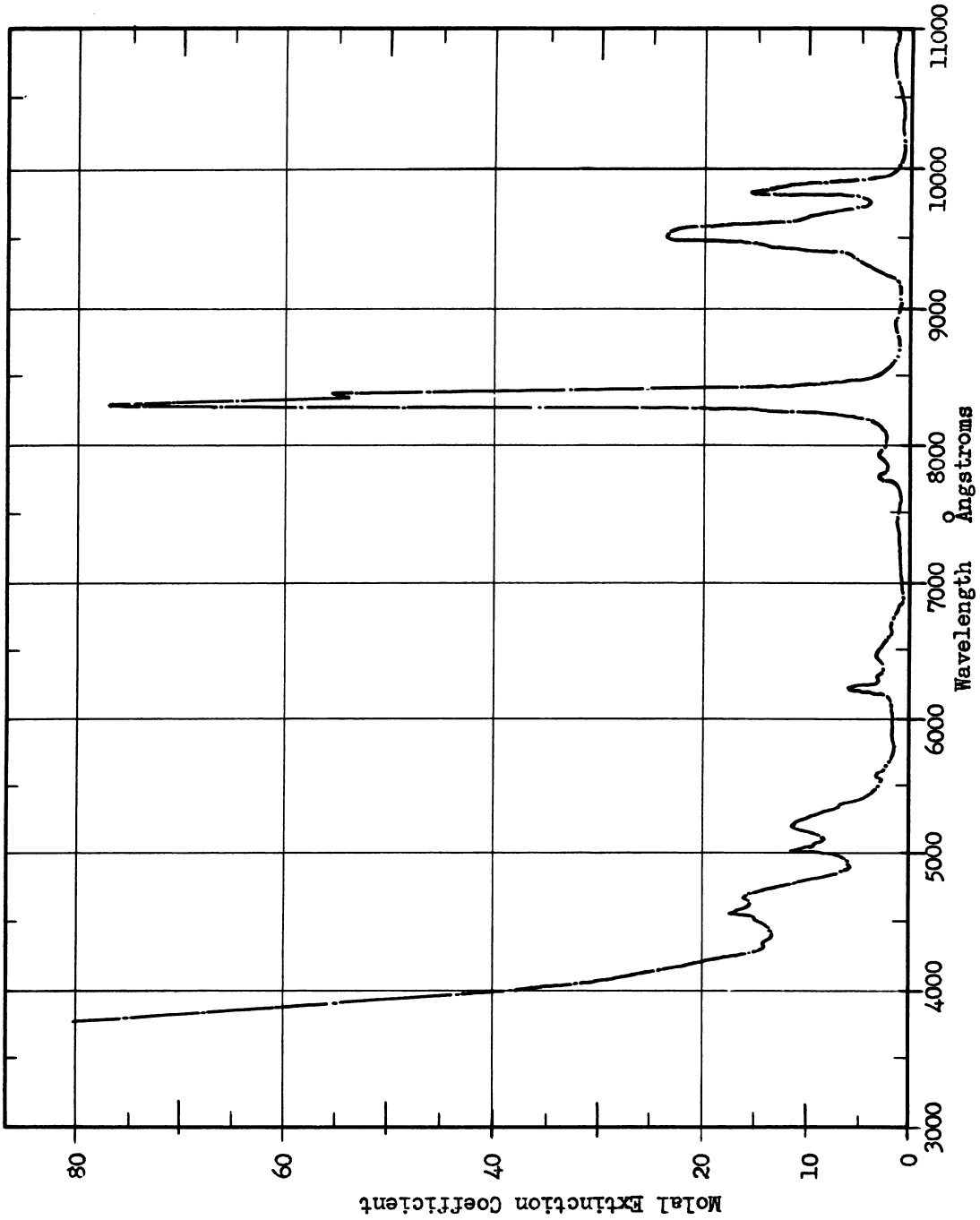

Fig. III-4. Absorption Spectrum of Pu(VI) in 0.5 M HCl

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organic solvents is discussed in Chapter V. Other specific properties and compounds of Pu(VI) are discussed in subsequent sections of this chapter.

Higher Oxidation States.— Attempts to prepare plutonium of oxidation number higher than (VI) either by oxidation with AgO in 1 M HNO_3 or by electrolytic oxidation in alkaline solution have not been successful.

OXIDATION AND REDUCTION OF PLUTONIUM

Oxidation Potentials and Equilibrium Constants

Disproportionation of Pu(IV).— The stability of Pu(IV) is such that it undergoes partial disproportionation into Pu(III) and Pu(VI) in dilute solutions of HCl, HNO_3 or $HClO_4$. The equilibrium concentrations of Pu(III), Pu(IV) and Pu(VI) in a 0.5 M HCl solution have been measured. The equilibrium constant for equation (1) defined in terms of molar concentrations by equation (2) is 0.052 in 0.5 M HCl at room temperature.

$$3\ Pu(IV) = 2\ Pu(III) + Pu(VI) \qquad (1)$$

$$K = \frac{[Pu(VI)]\ [Pu(III)]^2}{[Pu(IV)]^3} = 0.052 \qquad (2)$$

The equilibrium constant for the disproportionation reaction has approximately a fourth power hydrogen ion concentration dependence. The absorption spectrum of the equilibrium mixture of Pu(III), Pu(IV)

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and Pu(VI) resulting from the disproportionation of Pu(IV) in 0.5 M HCl is shown in Figure III-5.

Formal Oxidation Potentials of the Pu(III), Pu(IV) Couple.— In addition to the measurements on solutions containing plutonium in disproportionation equilibrium, a number of direct measurements of the oxidation potential of the $Pu(III) = Pu(IV) + e^-$ couple have been made in solutions containing various anions. These values are reported in Table III-1.

With a few exceptions, which are so indicated, the formal potential values listed in Table III-1 were calculated from observed e.m.f.'s of cells consisting of bright platinum electrodes in contact with the various plutonium solutions, and a saturated calomel reference electrode. In general, the measurements were made at approximately equal concentrations of Pu(III) and Pu(IV), the total plutonium concentration being from 0.01 to 0.02 molar. The actual concentration of Pu(III) and Pu(IV) was in each case determined spectrophotometrically with an error of not more than $\pm$ 3 per cent. The observed e.m.f. was corrected to a Pu(III):Pu(IV) ratio of unity, but no correction was made for the liquid junction potentials. The measurements were conducted on a 0.2 to 1 ml. scale. The observed e.m.f.'s were obtained under conditions where the Pu(III), Pu(IV) couple behaved reversibly, except in one case noted in the Table.

The potential of the Pu(III), Pu(IV) couple is independent of the pH when the pH is less than unity.

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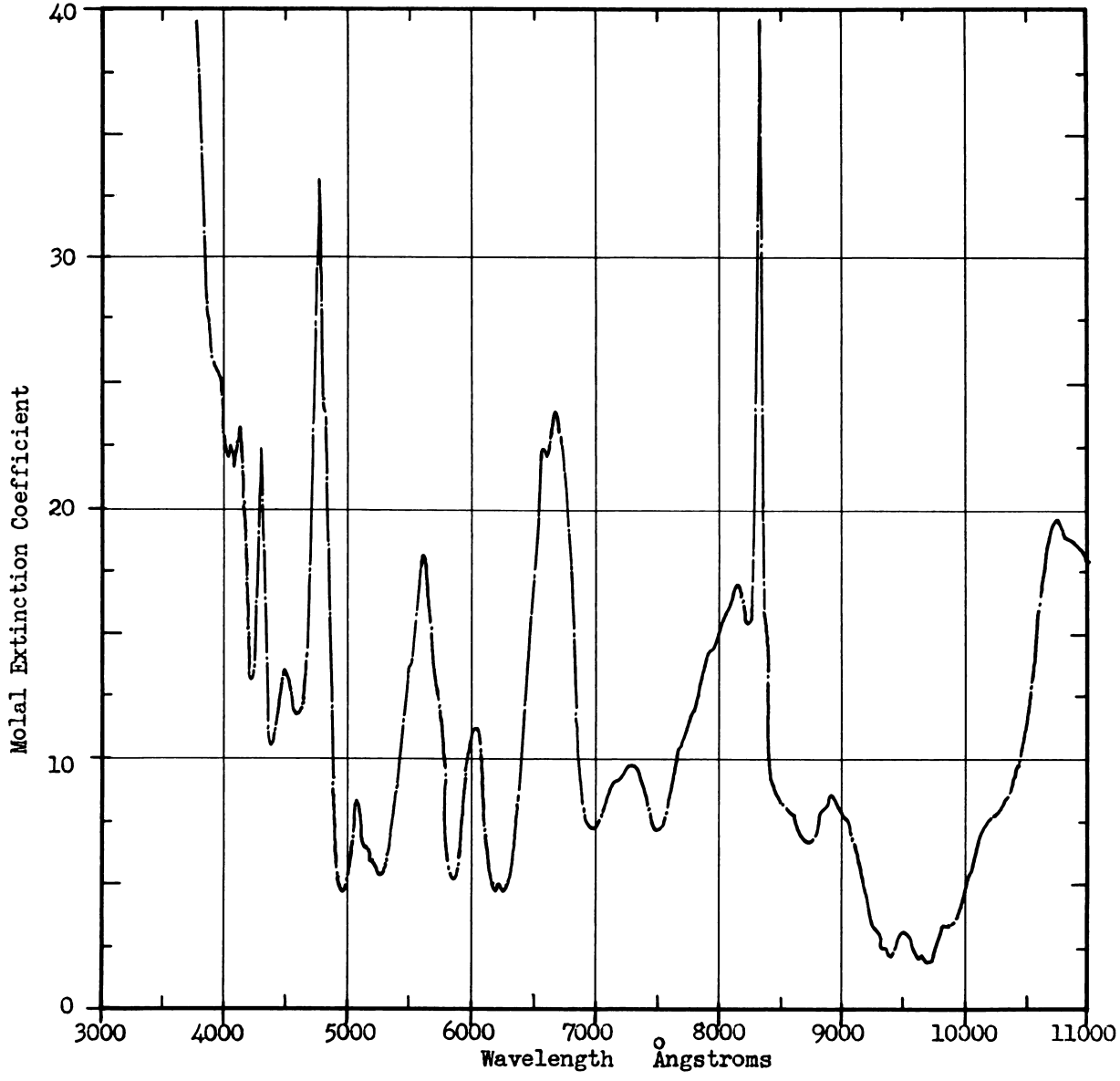

Fig. III-5. Equilibrium Mixture after Disproportionation of Pu(IV)

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Table III-1. Formal Oxidation Potentials for the Pu(III), Pu(IV) Couple

Medium	Oxidation Potential[a] (volts)
1.0 M $HClO_4$	-0.949 ± 0.005
2.0 M $HClO_4$	-0.957 ± 0.005
4.0 M $HClO_4$	-0.98 ± 0.01
1.0 M HCl - 1.0 M NaCl	-0.954 ± 0.005
1.0 M HCl	-0.966 ± 0.005
1.0 M HNO_3	-0.916 ± 0.006
1.0 M H_2SO_4	-0.75 ± 0.02
1.0 M HCl - 0.1 M H_3PO_4	-0.80
1.0 M HCl - 0.6 M H_3PO_4	-0.59
1.0 M HAc - 1.0 M NaAc	-0.40
0.05 M H_2SO_4 - 0.8 M $K_2C_2O_4$	-0.082[b]
0.2 M H_2SO_4 - 0.18 M $K_2C_2O_4$	-0.235[b]
9.0 M NH_4F - 0.05 M H_2SO_4	+0.8[c] (approx.)
0.2 M HaAc - 0.2 M HAc	-0.28
1.0 M HCl - 1.0 M HF	-0.53

[a] Potential in volts referred to the hydrogen electrode at 26 ± 2°C.

[b] Polarographically determined - reversible behavior.

[c] Polarographically determined - irreversible behavior.

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Oxidation Potentials of the (III), (IV) and (VI) States.-- Potential measurements in 1 molar acid solutions containing spectrophotometrically determined concentrations of Pu(III), Pu(IV) and Pu(VI) in disproportionation equilibrium have provided a basis for calculation of the formal oxidation potentials of couples involving these three oxidation states. In 1.0 M HCl at 25°C.:

$$Pu(III) \xleftrightarrow{-0.966\ v.} Pu(IV) \xleftrightarrow{-1.047\ v.} Pu(VI)$$
$$\uparrow \qquad\qquad -1.020\ v. \qquad\qquad \uparrow$$

A similar scheme for the system in 1.0 M $HClO_4$ at 25°C. is:

$$Pu(III) \xleftrightarrow{-0.945\ v.} Pu(IV) \xleftrightarrow{-1.067\ v.} Pu(VI)$$
$$\uparrow \qquad\qquad -1.027\ v. \qquad\qquad \uparrow$$

Graphical extrapolation of similar measurements made in 0.1 to 0.8 M HNO_3 give the following values for the couples at about 30°C. in 1 M HNO_3 :

$$Pu(III) \xleftrightarrow{-0.924\ v.} Pu(IV) \xleftrightarrow{-1.114\ v.} Pu(VI)$$
$$\uparrow \qquad\qquad -1.042\ v. \qquad\qquad \uparrow$$

Combining the formal potential for the Pu(III),Pu(IV) couple with equilibrium constants given in Eqs. (2) and (4) leads to the following potential scheme in 0.5 M HCl :

$$Pu(III) \xleftrightarrow{-0.967} Pu(IV) \xleftrightarrow{-1.097} Pu(V) \xleftrightarrow{-0.912} Pu(VI)$$
$$\downarrow \qquad\qquad\qquad\qquad -1.004 \qquad\qquad\qquad\qquad \downarrow$$

Measurements on solutions in disproportionation equilibrium indicate that a fourth power hydrogen ion function is involved in the variation with hydrogen ion concentration of the potentials of the Pu(III)-Pu(VI) and Pu(IV)-Pu(VI) couples. Since there is considerable

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chemical evidence that the PuO_2^{++} ion exists in acid solutions of Pu(VI), the probable reactions are:

$$Pu^{+3} + 2\ H_2O = PuO_2^{++} + 4\ H^+ + 3\ e^-$$

$$Pu^{+4} + 2\ H_2O = PuO_2^{++} + 4\ H^+ + 2\ e^-$$

Equilibria Involving Pu(V).— It is believed that the equilibrium for the following reaction has been measured:

$$Pu(V) + Pu(IV) = Pu(III) + Pu(VI) \qquad (3)$$

A solution containing all four oxidation states was prepared by the electrolytic reduction to Pu(V) of approximately 50 per cent of the plutonium in a Pu(VI) solution in 0.5 N HCl. The Pu(V) is thermodynamically unstable in this solution with respect to disproportionation into Pu(VI) and Pu(IV) and it was found that the Pu(V) slowly disappeared over a period of several hours. However, the disproportionation of Pu(V) gave rise initially to Pu(III) and Pu(VI), rather than Pu(IV) and Pu(VI) which are the principal stable end products of the disproportionation. The most reasonable explanation is that Pu(IV) and Pu(VI) are actually formed from the Pu(V) disproportionation but that any Pu(IV) thus formed is used up by reaction with Pu(V) according to equation (3).

As the disproportionation of the Pu(V) proceeded further, it was found that appreciable concentrations of Pu(IV) began to appear. Since the reaction between Pu(IV) and Pu(V) must be quite rapid, in that no

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Pu(IV) appeared initially, the appearance of both Pu(IV) and Pu(III) indicates that the actual equilibrium of equation (3) was established. By spectrophotometric measurements of the concentrations of the four oxidation states during the course of the experiment, it was possible to obtain values for the equilibrium constant of equation (3) over a considerable range of concentrations of the different oxidation states. Table III-2 gives a summary of these measurements.

Table III-2.

Relative Concentrations of Various Oxidation States at Different Times

Time in Hours	Plutonium Oxidation State, Per Cent of Total Plutonium					Equivalents Reduced	K
	(VI)	(V)	(IV)	(III)	Total		
1.0	48.1	45.3	1	2.4	95.8	52.5	--
3.0	55.2	38.0	1	4.7	98.9	54.1	--
5.0	62.3	29.6	2.0	7.2	101.1	55.2	7.6
7.0	68.5	20.8	3.7	9.3	102.3	56.1	8.3
9.0	72.5	14.2	5.8	9.8	102.3	55.2	8.6
11.0	74.5	10.0	8.0	9.5	102.0	54.5	8.8
13.0	75.6	7.8	9.6	8.5	101.5	52.5	8.6
15.0	76.4	6.3	11.4	7.7	101.8	52.2	8.2
17.0	76.8	5.2	12.9	7.1	102.0	52.3	8.1
19.0	77.0	4.5	14.0	6.6	102.1	52.3	8.1
24.0	76.5	3.6	16.5	5.1	101.7	51.9	6.6
29.0	76.0	3.0	18.8	4.0	102.8	52.6	5.4
39.0	75.1	1.5	21.7	3.0	101.3	53.9	6.9

The first column in Table III-2 shows the time elapsed after the conclusion of the electrolytic reduction of the Pu(VI). The constant K

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tabulated in the last column of the Table is defined by the equation:

$$K = \frac{[Pu(III)]\ [Pu(VI)]}{[Pu(V)]\ [Pu(IV)]} \qquad (4)$$

Within the experimental error the values of K obtained are constant, thus giving supporting evidence to the belief that the actual equilibrium of equation (3) was being measured.

Oxidation - Reduction Reactions

Oxidation of Pu(III) to Pu(IV).—

1. Oxygen. The oxidation of Pu(III) to Pu(IV) by O_2 is of very great importance in the chemistry of Pu(III). The potential in HCl and $HClO_4$ solutions for the Pu(III), Pu(IV) couple is ca. -0.96 volts and, as would be expected, the oxidation by O_2 in these solutions is very slow. This is to be ascribed to the mechanism of oxidation by O_2 in acid solution which is known, in general, to involve the formation of H_2O_2 as the first step. The potential for the formation of H_2O_2 from O_2 is only -0.69 volts so that it is not surprising that the oxidation of Pu(III) by O_2 in acid solution is slow.

Experimental proof of the slowness of oxidation of Pu(III) by O_2 in acid solution was obtained in the following experiments. A Pu(III) solution free of oxidizing or reducing agents was prepared in 0.5 M HCl; the solution was saturated by bubbling O_2 through it and then allowed to stand at room temperature for 42 hours. Less than one per cent oxidation occurred as measured spectrophotometrically.

Another 0.5 N HCl solution of Pu(III) free from oxidizing or

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reducing agents was sealed in a cone under 1 atmospheric pressure of O_2. The cone was then heated for 4 hours at 97°C. On analyzing the solution spectrophotometrically, less than 2 per cent of the plutonium was found to have been oxidized.

The presence of sulfuric acid in a solution of Pu(III) seems to greatly increase the rate of oxidation by O_2. A Pu(III) solution in 0.2 N H_2SO_4 is largely oxidized in the course of a few days. This effect of H_2SO_4 is probably connected with its stabilizing action on the Pu(IV) state which shifts the Pu(III), Pu(IV) potential to about -0.75 volts (see Table III-1). This, in turn, would be expected to give rise to a more rapid rate of oxidation by O_2 as discussed above.

When a solution of Pu(III) is made basic, a very rapid oxidation by O_2 takes place. Thus, only mixed hydroxides of Pu(III) and Pu(IV) are precipitated when hydroxide is added to a Pu(III) solution in the presence of air.

2. Nitric Acid. The HNO_3 oxidation of Pu(III) to Pu(IV) is of interest because HNO_3 solutions of Pu(III) are commonly employed. Concentrated HNO_3 oxidizes Pu(III) to Pu(IV) very rapidly; dilute HNO_3 oxidizes Pu(III) slowly. The reaction is probably autocatalytic so that until a careful study is made of the system it is difficult to predict the rate under various conditions.

3. Dichromate and Chlorine. Dichromate brings about very rapid oxidation of Pu(III) to Pu(IV) in 0.5 M HNO_3 solution.

The oxidation of Pu(III) by Cl_2 in dilute HCl is not immediate but proceeds at a measurable rate. A solution in 0.5 M HCl with an

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initial Pu(III) concentration 5.2×10^{-3} molar and chlorine concentration 8.3×10^{-3} molar was 50 per cent oxidized in approximately two days.

Oxidation of Pu(IV) to Pu(VI).--

1. Nitric Acid. Because of the extensive use of HNO_3 solutions as a solvent for plutonium, some investigations of the oxidation of Pu(IV) by HNO_3 have been made. It has been observed that the oxidation in dilute HNO_3 solutions proceeds at a moderate rate at elevated temperatures. The rate falls off rapidly with increasing HNO_3 concentration. This effect may be attributed in part to the stabilization of the Pu(IV) by the formation of the $[Pu(NO_3)_6]^{--}$ complex. It may also be caused by a decreased rate of disproportionation at higher hydrogen concentrations, if the mechanism of oxidation involves disproportionation.

2. Oxygen. The oxidation of Pu(IV) to Pu(VI) by O_2, although thermodynamically possible, seems to be extremely slow both in acid and alkaline solution. A Pu(IV) solution was made 0.25 M in NaOH and the precipitated hydroxide was allowed to stand in contact with the solution for 24 hours with occasional stirring. No change in the character of the precipitate was observed. On dissolving the precipitate in HCl and analyzing the solution little, if any, oxidation was found to have occurred. Similar experiments in 0.25 M NaOH and 1.0 M NaOH solutions heated at 100°C. for 4 hours and 2 hours, respectively, also gave no evidence of oxidation to Pu(VI).

3. Oxidation Mechanism. In the case of some reagents which oxidize Pu(IV) to Pu(VI) slowly, it is very probable that the mechanism of the oxidation involves the oxidation of Pu(III), present due to disproportionation, to Pu(IV) and the simultaneous disproportionation of more Pu(IV)

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into Pu(VI) and Pu(III). By such a mechanism the Pu(IV) would be eventually completely oxidized to Pu(VI). It is important, therefore, that the order of the rate of oxidation with respect to the concentration of plutonium be determined. If the above mechanism is correct, the rate will greatly decrease with decreasing plutonium concentration and could be estimated from rate of disproportionation data. There is qualitative evidence that this mechanism may be followed in both the oxidation of Pu(IV) by HNO_3 and by dichromate.

Reduction of Pu(IV) to Pu(III).-- Both NH_2OH and SO_2 readily reduce Pu(IV) to Pu(III). Hydrogen peroxide, iodide ion, and $H_2C_2O_4$ are also capable of reducing Pu(IV) to Pu(III). Oxalic acid brings about reduction in dilute HCl solutions but not in dilute H_2SO_4 solutions in the presence of O_2. A very useful reducing agent is H_2 gas. No appreciable reduction takes place on bubbling H_2 through a solution of Pu(IV) and only slow reduction when H_2 is bubbled through the solution in the presence of a piece of shiny platinum. However, in the presence of platinized platinum the reduction takes place quite rapidly. In this manner a Pu(III) solution free from reducing and oxidizing agents may be readily prepared. Stannous ion reduction of Pu(IV) is complete and has been used in titrations to determine the Pu content.

Reduction of Pu(VI) to Pu(IV).-- Plutonium(VI) is reduced to Pu(IV) by fuming with concentrated H_2SO_4. It was found necessary to fume the solution very strongly and for long periods of time to obtain complete reduction. The times of fuming and the per cent reduction observed in one such experiment are presented in Table III-3.

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Table III-3. Reduction of Pu(VI) by Fuming with H_2SO_4

Time of Fuming	Per cent Reduction
15 min.	8
60 "	20
70 "	36
115 "	82

It was necessary to add more H_2SO_4 from time to time; therefore, the values at different times are not strictly comparable.

Reduction of Pu(VI) to Pu(V).-- Plutonium(VI) can be partially reduced to Pu(V) electrolytically using a platinum cathode and a divided cell. Plutonium(V) is also readily produced by the reduction of Pu(VI) in dilute acid solution by the following reducing agents: SO_2, NH_3OHCl, H_2O_2, Ag and H_2 with platinized platinum catalyst. In some cases, further reduction of the Pu(V) is brought about if an excess of reducing agent is present. In every case the Pu(V) is thermodynamically unstable and therefore decomposes slowly.

Reduction of Pu(VI) to Pu(III).-- The reagents NH_3OH^+, SO_2, Ag and H_2 with platinized platinum catalyst all reduce Pu(VI) eventually to Pu(III) in dilute acid. In each case Pu(V) can be detected as an intermediate state in the reduction.

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IONIC SPECIES IN SOLUTION AND COMPLEX FORMATION

The nature of the ions of plutonium which exist in solution has been investigated by various methods. Measurements of the oxidation potential of the Pu(III), Pu(IV) couple which have been reported in Table III-1 of the preceding section, and the solubility data reported in Table III-8 of the subsequent section, lead to certain conclusions concerning the nature of plutonium ions in solution. Additional information has been obtained by studying the absorption spectra of various solutions of plutonium and by determining the electrical migration of plutonium ions under various conditions. Absorption spectra and electrical migration data are presented in this section in connection with a unified discussion of the nature of plutonium ions in solution.

Electrical Migration of Plutonium Ions

Experimental Technique.-- In order to obtain electrical migration data, Pyrex cells were constructed consisting in principle of a center compartment separated from the anode and cathode compartments by means of sintered glass discs to prevent mechanical mixing of the solutions. The particular solution to be investigated was placed in the cell and plutonium was added only to the solution in the middle compartment. The anode and cathode compartments were constructed in the form of H cells and the electrodes were placed in one arm of these units. Whenever the acidity of the solution permitted, copper electrodes were

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used and a saturated solution of the appropriate copper salt was placed in the electrode arm of the H cell so that electrolysis in these compartments could proceed without gas evolution or change in pH. In solutions where copper could not be used, platinum electrodes were employed.

In general, a current of 5 to 10 milliamperes was passed for a period of 16 to 18 hours. After passage of the current, the anode and cathode compartments were assayed for plutonium radiochemically to determine the amount of plutonium which had migrated. This amount was usually from 1 to 50 per cent of the total plutonium originally present in the central compartment and the original plutonium concentration was generally of the order of 0.5 gram per liter. The percentages of the total amount of plutonium which had migrated, found in the cathode and anode compartments, are reported as the significant data from the experiments.

Measurements in fluoride solutions were performed in a paraffined cell employing hardened filter paper diaphragms in place of sintered glass discs.

Electrical Migration Data.--- The results obtained using the technique described above are reported in Table III-4. Except where noted in the Table, it is believed that the possible error due to diffusion can be neglected in interpreting the results.

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Table III-4

Electrical Migration of Plutonium in Solutions Containing Various Anions

Oxidation State	Solution	Distribution of Migrating Pu		Nature of Pu ion
		% to cathode	% to anode	
III	1 M HCl	79.5*	20.5	Cation primarily
III	10 M HCl	69.5	30.5	" "
III	0.5 M H_2SO_4	97	3	Cation
III	1 M H_2SO_4	46	54	Cation, anion both present
III	4 M H_2SO_4	46	54	Doubtful due to diffusion
IV	1 M HNO_3	99	1	Cation
IV	4 M HNO_3	99	1	Cation
IV	8 M HNO_3	13	87	Anion
IV	10 M HNO_3	1.2	98.8	Anion
IV	10 M $HClO_4$	95.7	4.3	Cation
IV	2 M HCl	99.95	0.05	Cation
IV	4 M HCl	93.5	6.5	Cation
IV	7 M HCl	7	93	Anion
IV	10 M HCl	0.3*	99.7	Anion
IV	0.1 M H_2SO_4	25	75	Anion
IV	0.5 M H_2SO_4	6	94	Anion
IV	1.0 M H_2SO_4	1	99	Anion
IV	1 M HNO_3, 0.01 M HF	100	0	Cation

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Table III-4, Continued

Oxidation State	Solution	Distribution of Migrating Pu		Nature of Pu ion
		% to cathode	% to anode	
IV	1 M HNO_3, 1 M HF	93	7	Cation
IV	0.1 M HNO_3, 1 M HF	99	1	Cation
IV	Sat. NH_4F plus 1/9 vol 10 M HNO_3, pH = 5	91	9	Cation
IV	0.1 M $H_2C_2O_4$, 0.1 M HNO_3	1	99	Anion
IV	0.1 M $H_2C_2O_4$, 1.0 M HF, 1.0 M HNO_3	60	40	HF destroys the oxalate complex (?)
IV	1.2 M H_3PO_4, 2 M $HClO_4$	90.5	9.5	Cation
IV	1.1 M HAc, 0.06 M NaAc, 1.1 M $NaNO_3$, pH = 3.5	1.8	98.2	Anion

* Average of two determinations where the precision was within one per cent.

The data in Table III-4 are considered in connection with the other data bearing on the nature of plutonium ions in the discussion which follows.

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Ionic Species and Complexes of Pu(III)

Uncomplexed Pu(III).— The absorption spectra of Pu(III) in one molar solutions of HCl, $HClO_4$, H_2SO_4 or HNO_3 shown in Figures III-6 to III-9 are closely similar, suggesting that the same ion species, presumably hydrated Pu(III) is present in all these solutions.

Sulfate Complexes.— The absorption spectrum of Pu(III) in 1 M H_2SO_4 (Figure III-8) does not differ sufficiently from that in 1 M HNO_3 or 1 M HCl to warrant postulating a sulfate complex of Pu(III), although the increase in the solubility of $PuPO_4$ in increasing concentrations of H_2SO_4 as compared to the increase in solubility in increasing concentrations of HNO_3 (Table III-8), as well as the very low migration and increased transfer to the anode in 4 M H_2SO_4 evident from Table III-4, suggest complex formation.

Oxalate Complexes.— It has been noted that if the green plutonium(III) oxalate is treated with a saturated $K_2C_2O_4$ solution, the solid oxalate readily dissolves to give a clear green solution. This may be taken as evidence for complex formation.

Ionic Species and Complexes of Pu(IV)

Uncomplexed Pu(IV).— Absorption spectra of Pu(IV) in 1 to 10 M $HClO_4$ and in 0.3 to 4 M HCl shown in Figures III-10 and III-11 suggest that the same ion is present in all of these solutions, although there is evidence of appreciable complex formation as the HCl concentration is raised above two molar.

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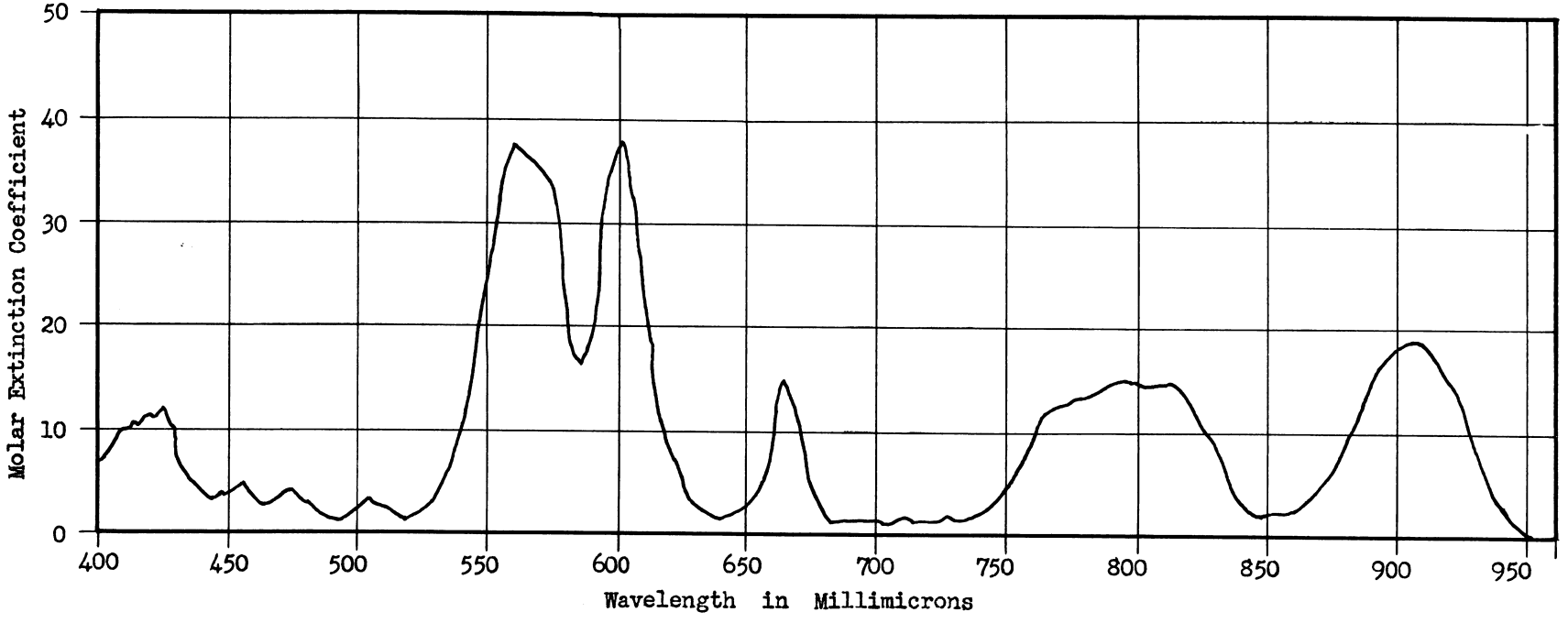

Fig. III-6. Absorption Spectrum of Pu(III) in 1 M HCl

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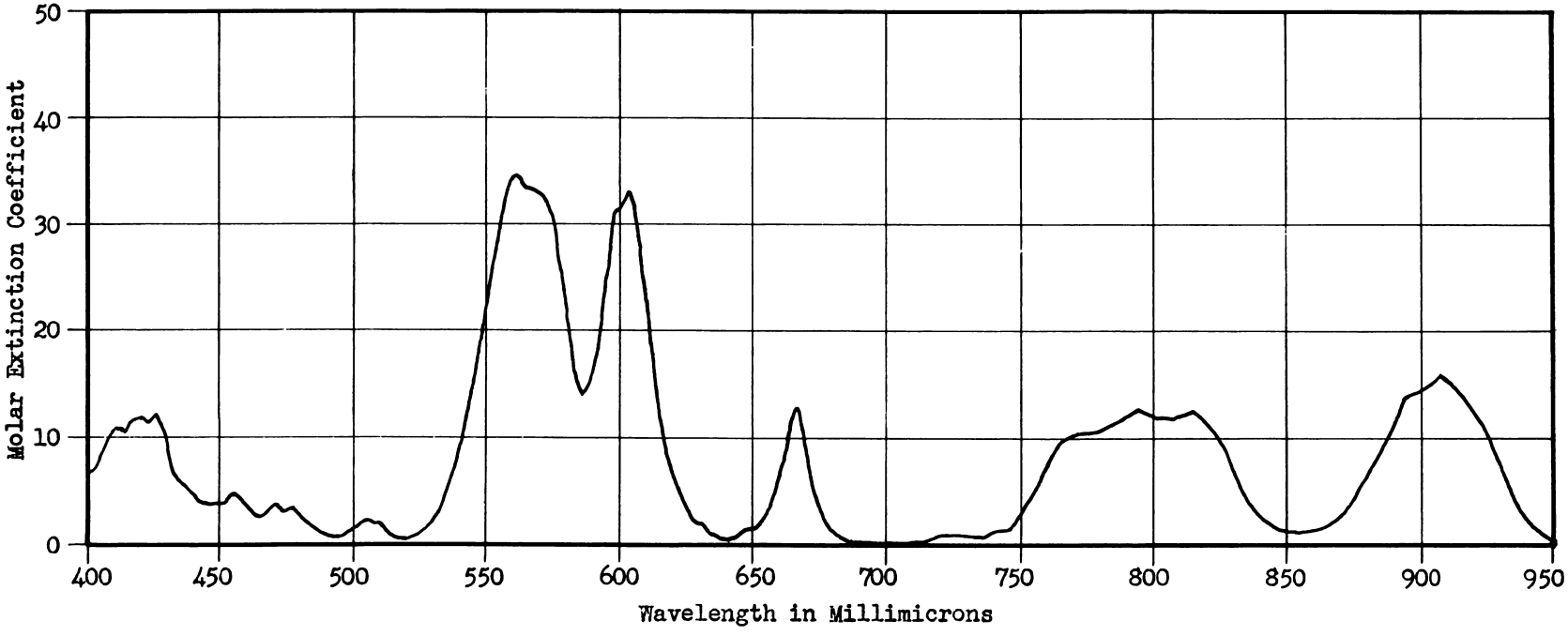

Fig. III-7. Absorption Spectrum of Pu(III) in 1 M $HClO_4$

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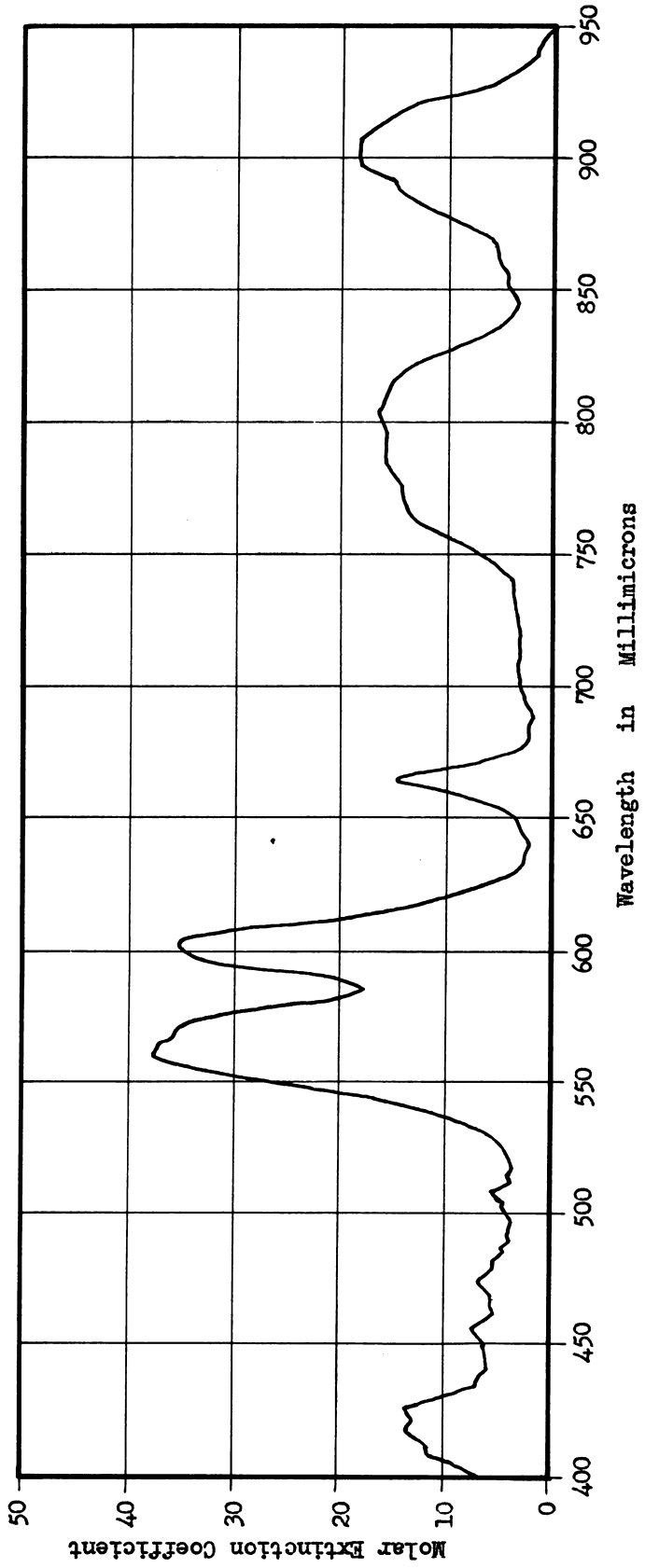

Fig. III-8. Absorption Spectrum of Pu(III) in 1 M H_2SO_4

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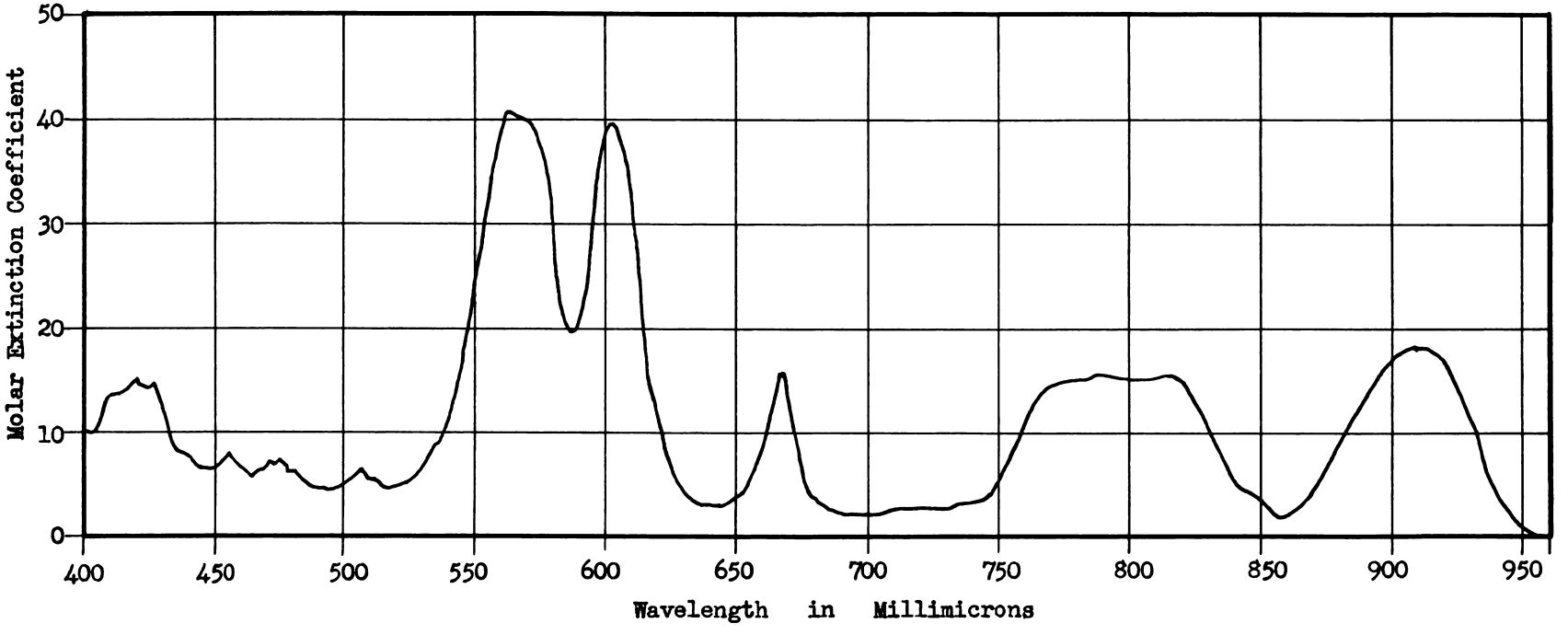

Fig. III-9. Absorption Spectrum of Pu(III) in 1 M HNO_3

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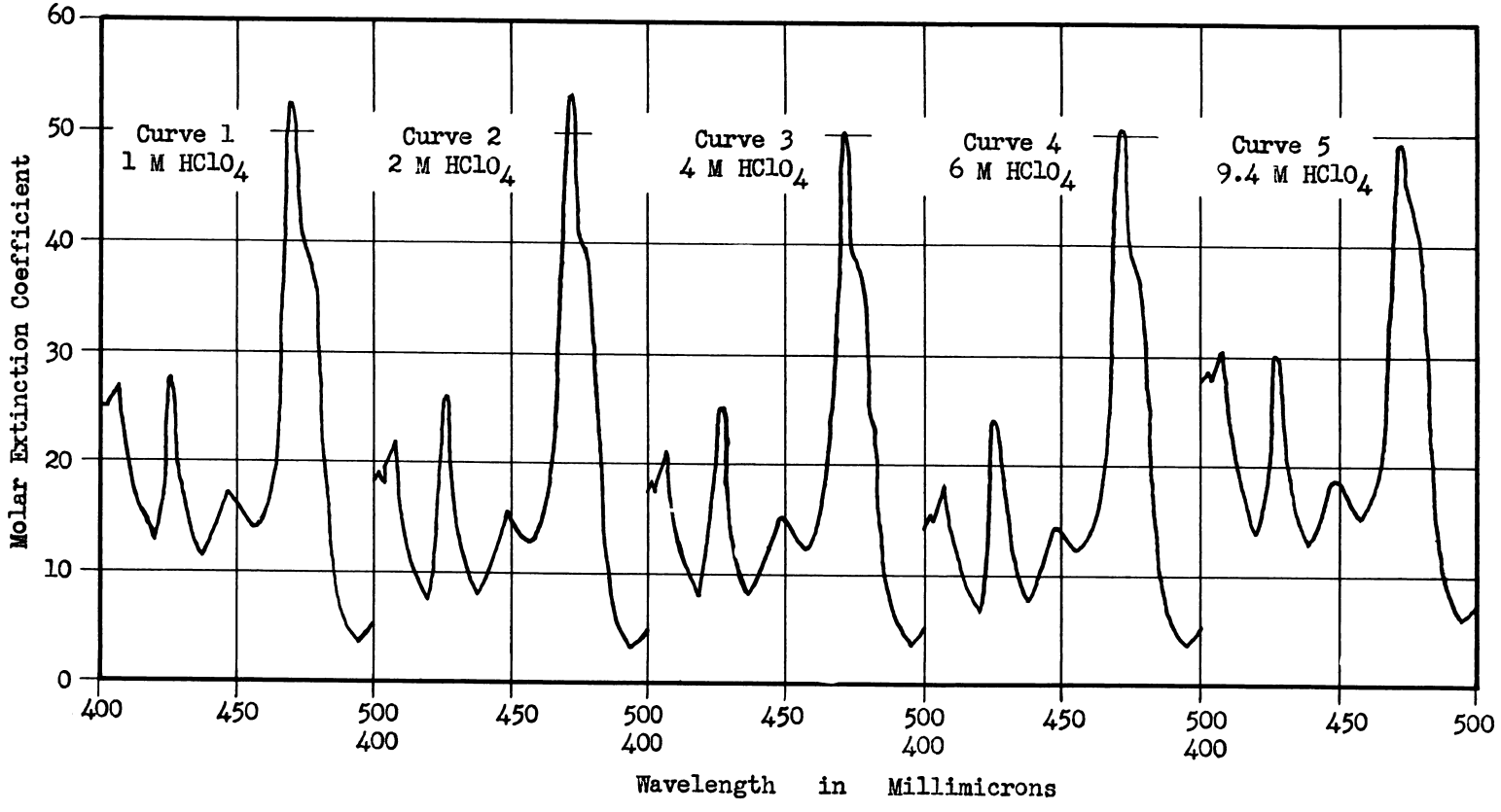

Fig. III-10. Absorption Spectrum of Pu(IV) in $HClO_4$

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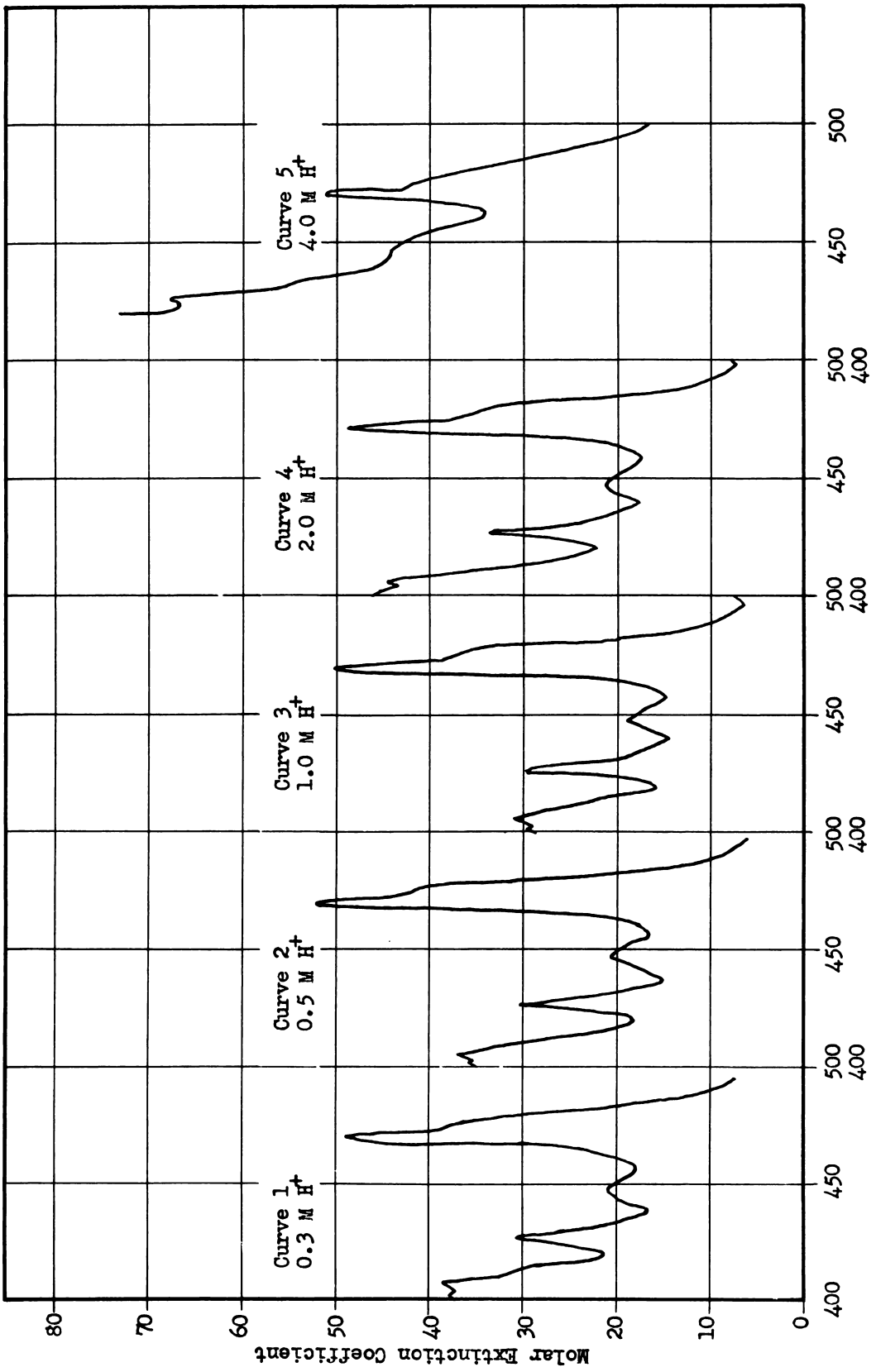

Fig. III-11. Absorption Spectrum of Pu(IV) in HCl

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Electromotive force measurements (Table III-1) show that the potential of the Pu(III), Pu(IV) couple in 1 M HCl is -0.966 volts and in 1 M $HClO_4$ it is -0.949 volts. Since perchlorate ion has little or no complexing power, the E'_o = -0.949 volts can be taken as the formal potential of the couple for the uncomplexed Pu(III) and Pu(IV) ions in one molar solution. A weak chloride complex of Pu(III) would be indicated by the 16 millivolts difference in the formal potentials between perchlorate and chloride solutions. If the measured oxidation potential for the couple in 1 M HNO_3 is corrected for the formation of the weak nitrate complex of Pu(IV), discussed below, a value of -0.945 volts is obtained. This value is within the experimental error of that measured in 1 M $HClO_4$.

Nitrate Complexes.— The existence of a complex cation and a complex anion of Pu(IV) and nitrate has been established by a consideration of the absorption spectra shown in Figure III-12 and the electrical migration data in Table III-4. Plots of the molar extinction coefficients for the 476 and 855 millimicron absorption bands which are characteristic of the complex cation, against the log y, the nitrate concentration, show the plutonium to be almost completely in the form of this ion in 2 molar nitrate, while the complex anion assumes increasing importance in the region from 4 to 11 molar nitrate. The formula of the complex cation was investigated by spectrophotometric analysis for the ion in 2 molar hydrogen ion with varying ratios of nitrate to chloride. Calculations from the data summarized in Table III-5 reveal that the number of nitrate ions involved in the formation of the first nitrate complex is between one and two, representing the formation of the ions $Pu(NO_3)^{+3}$ and $Pu(NO_3)_2^{+2}$, respectively.

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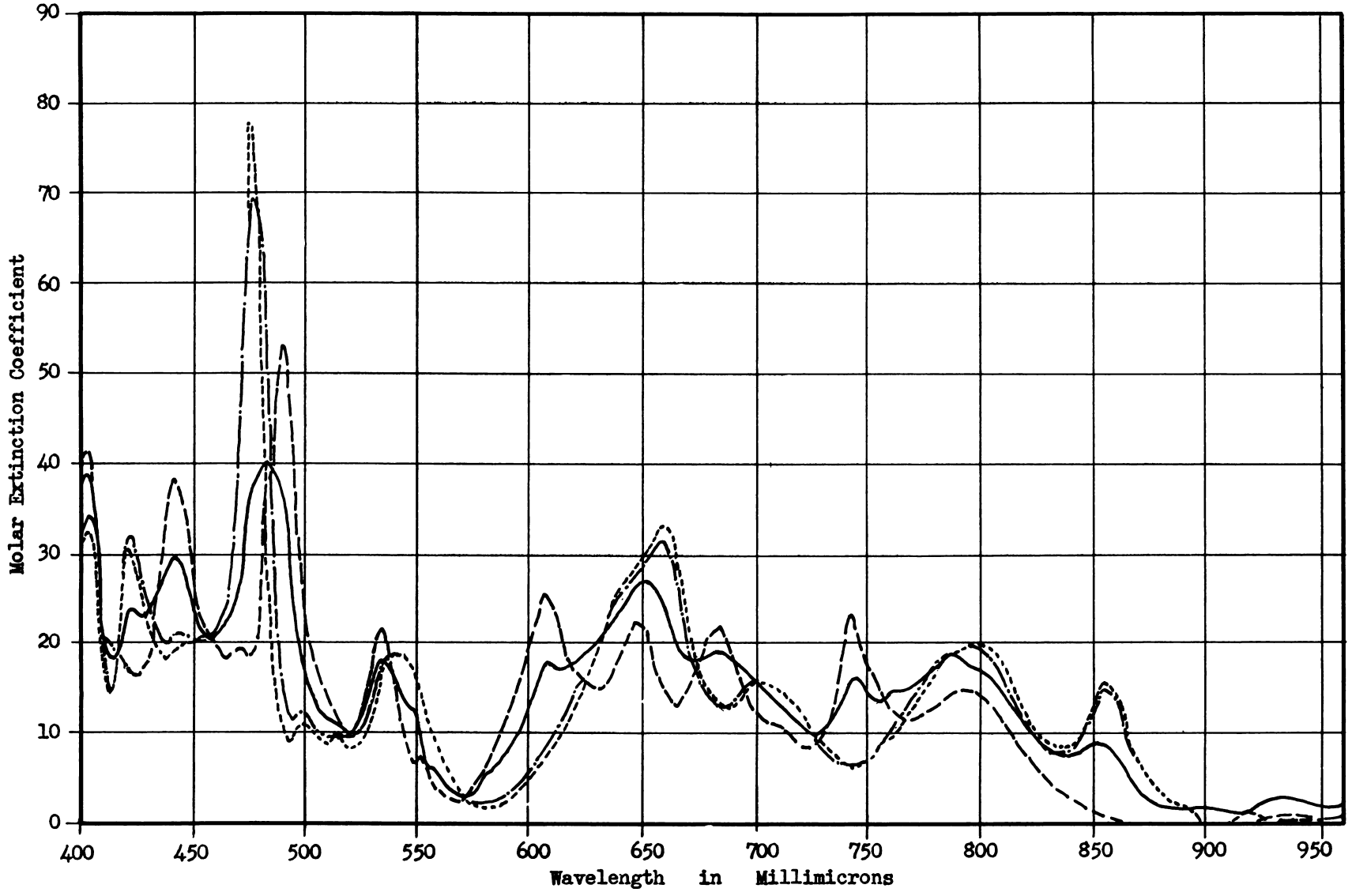

Fig. III-12. Absorption Spectrum of Pu(IV) in HNO_3

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Table III-5.

Variation of the Concentration of the Plutonium Nitrate Complex Cation with Nitrate Concentration at Constant Ionic Strength

HNO_3 (M)	2.00	1.00	1.00	0.55	0.50	0.25	0.20	0.12	0.11	0
HCl (M)	0	1.00	1.00	1.50	1.50	1.80	1.80	1.90	1.90	2.00
E* 477	78	74.3	72.8	63.6	62.0	52.5	51.0	43.6	42.9	35
% $Pu(NO_3)_x^{+(4-x)}$	(100)	91.5	88	66.4	62.9	40.8	37.3	20.9	18.6	0
k_1' (x = 1)		10.8	7.3	3.6	3.4	2.8	3.0	2.2	2.1	
k_1'' (x = 2)		10.8	7.3	6.6	6.8	11.1	14.9	18.3	18.9	
HNO_3 (M)	2.0	1.50	1.00	0.50	0.20	0.11	0			
$HClO_4$ (M)	0	0.50	1.00	1.50	1.82	1.90	2.0			
E* 477	78	75.9	75.2	69.7	57.0	48.9	39.5			
% $Pu(NO_3)_x^{+(4-x)}$	(100)	94.6	93.1	78.4	45.8	24.7	0			
k_1' (x = 1)		11.7	13.5	7.3	4.2	3.0				
k_1'' (x = 2)		7.8	13.5	14.6	21.1	27.2				

* Molar extinction coefficient.

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The uncertainty as to the exact formula of the complex cation arises from at least two sources: (1) the sensitivity of the calculated values of the constants k_1' and k_1'' to small changes in the measured extinction coefficients. This effect is particularly marked at very high ratios of complex ion to uncomplexed Pu^{+4} or of Pu^{+4} to complex ion. (See Table III-5.) (2) Specific ion effects; i.e., the (possibly large) effect on the ion activity coefficients as the solvent changes from ca. 2 M HNO_3 to ca. 2 M HCl or $HClO_4$.

The possibility of the formation of an ion such as $Pu_2(NO_3)_3^{+5}$ is not, of course, prohibited by these data, but until further work has been done should be considered as only a secondary possibility.

The formula of the nitrate complex which exists as an anion has been inferred from the following observations:

(1) In solutions containing 13 molar hydrogen ion and various nitrate to perchlorate concentration ratios, an increase in nitrate concentration results in the formation of a new ionic species having a characteristic absorption spectrum.

(2) Five or more nitrate groups must be attached to the Pu(IV) since the migration data in Table III-4 show that the plutonium is present as an anion in 10 M HNO_3.

(3) It is possible to crystallize from a 10 to 13 M HNO_3 solution containing ammonium ion and Pu(IV), the plutonium analogue of $(NH_4)_2Ce(NO_3)_6$. Since the existence of the cerium(IV) salt has been correlated with the existence in solution of the ion $Ce(NO_3)_6^{--}$, it seems reasonable to conclude that a complex anion of Pu(IV) and nitrate is $Pu(NO_3)_6^{--}$.

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Sulfate Complexes.-- Oxidation potentials of the Pu(III), Pu(IV) couple in 1 M H_2SO_4 given in Table III-2 show that Pu(IV) is strongly complexed in this solution. Absorption spectra in Figures III-13 and III-14 would indicate that at least three complex ions of sulfate and Pu(IV) are formed. Preliminary work has established the presence of a $Pu(SO_4)^{+2}$ and possibly a $Pu_2(SO_4)_3^{++}$ ion in solutions of 1 molar hydrogen ion concentration and 0.1 molar bisulfate ion concentration. The formation of a complex anion of Pu(IV) and sulfate is indicated by the migration data in Table III-4.

Oxalate Complexes.-- The formulas of two of the various oxalate complexes of Pu(IV) have been determined by studying the solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in 0.75 M HNO_3 at various oxalic acid concentrations. These solubility data are summarized in Table III-6.

Table III-6.

Solubility of $Pu(C_2O_4) \cdot 6H_2O$ in 0.75 M HNO_3 and Various Oxalic Acid Concentrations

Conc. $H_2C_2O_4$ moles/liter	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$, mg/liter	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$, moles/liter
0.40	117	4.89×10^{-4}
0.196	60.7	2.54×10^{-4}
0.145	48.8	2.04×10^{-4}
0.0941	33.2	1.39×10^{-4}
0.0433	19.7	8.26×10^{-5}
0.0179	12.5	5.21×10^{-5}
0.0068	10.1	4.21×10^{-5}

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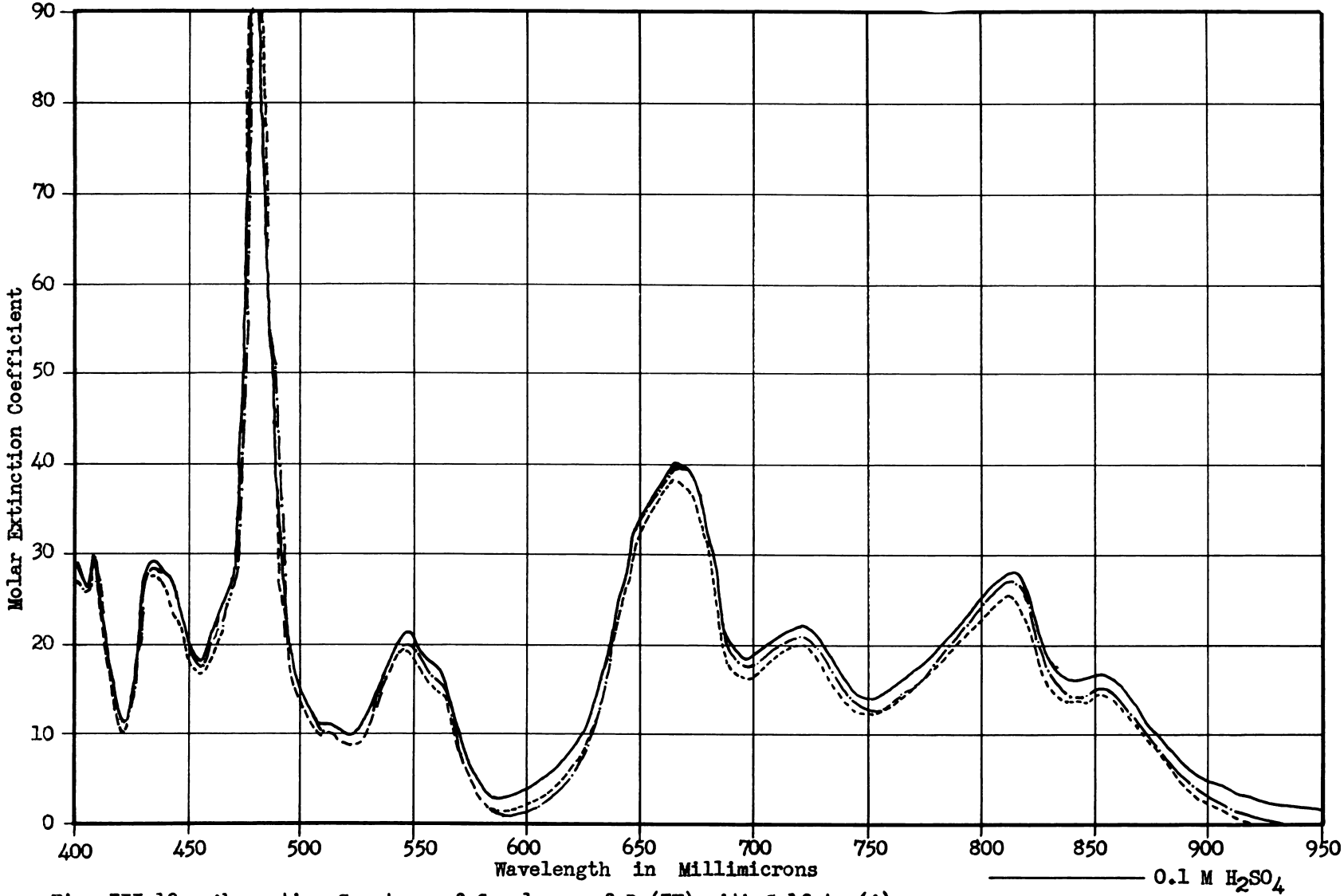

Fig. III-13. Absorption Spectrum of Complexes of Pu(IV) with Sulfate (A)

(Peak E = 112.5 at 480.5 millimicrons)

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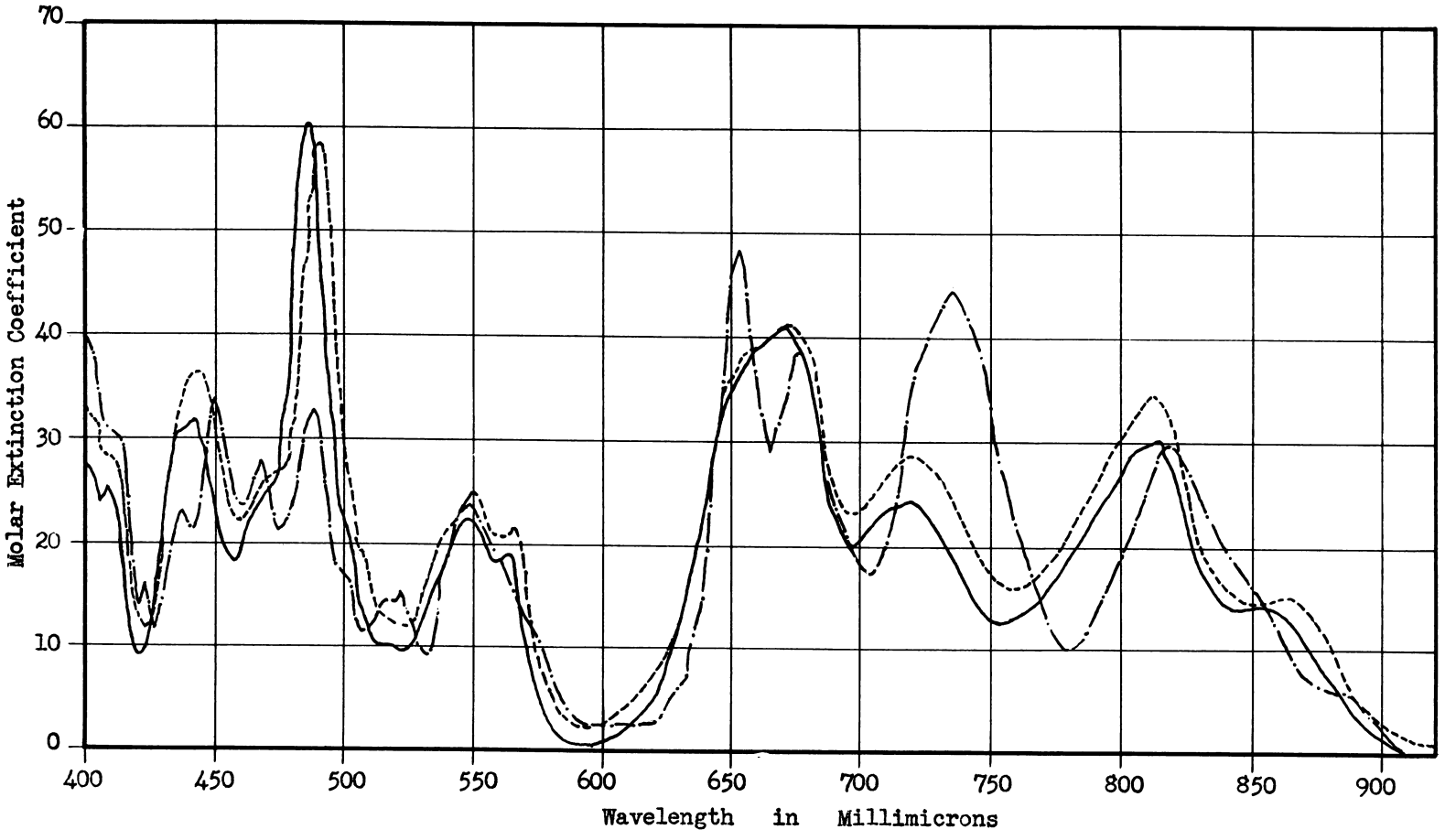

Fig. III-14. Absorption Spectrum of Complexes of Pu(IV) with Sulfate (B)

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The equilibria in solution may be expressed by the following equations:

$$Pu(C_2O_4)_2 \cdot 6H_2O(s) = Pu(C_2O_4)_2(aq) + 6H_2O \quad (5)$$

$$Pu(C_2O_4)_2 \cdot 6H_2O(s) + H_2C_2O_4 = Pu(C_2O_4)_2^{--} + 2H^+ + 6H_2O \quad (6)$$

The equilibrium constants for equations (5) and (6) are:

$$K_1 = \left[Pu(C_2O_4)_2(aq)\right] = 3.14 \times 10^{-5} \quad (7)$$

$$K_2 = \frac{\left[Pu(C_2O_4)_3^{--}\right]\left[H^+\right]^2}{\left[\Sigma\, H_2C_2O_4\right]^*} = 6.5 \times 10^{-4} \quad (8)$$

The percentage of Pu(IV) existing as $Pu(C_2O_4)_3^{--}$ in 0.75 M HNO_3 and various oxalic acid concentrations will be found in Table III-7.

Table III-7.

The Percentage of Pu(IV) Existing as $Pu(C_2O_4)_3^{--}$ in Various Oxalic Acid Solutions (0.75 M HNO_3)

$H_2C_2O_4$ moles/liter	% Pu(IV) as $Pu(C_2O_4)_3^{--}$
0.4	93.5
0.1	78.6
0.01	27.0
0.001	3.5

* $\left[\Sigma\, H_2C_2O_4\right]$ is defined as follows:

$$\left[(\Sigma\, H_2C_2O_4)\right] = \left[(H_2C_2O_4)\right] + \left[(HC_2O_4^-)\right]$$

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As far as is known, $Pu(C_2O_4)_4^{-4}$ exists only in solutions of ammonium or alkali oxalates.

Acetate Complex.-- If a solution of plutonium(IV) is treated with excess sodium acetate, the color of the solution changes from green or brown to purplish orange. A concentrated solution(> 0.1 molar) of the plutonium(IV) acetate complex appears to be unstable, for when the solution is allowed to stand a pink precipitate, presumably a basic acetate, slowly forms.

The complex anion of Pu(IV) in acetate indicated by the migration data in Table III-4 has a distinct absorption spectrum as evidenced by Figure III-15.

Citrate Complex.-- Plutonium(IV) iodate has been dissolved in a sodium citrate solution to give a clear orange solution, indicating the existence of a citrate complex of Pu(IV).

Hydrolytic Behavior of Pu(IV).-- Spectrophotometric evidence that the ionic species of Pu(IV) in solutions of 0.3 M HCl is the same as the species in 10 M $HClO_4$ is inferential evidence that no hydroxyl groups are attached to the Pu(IV) ion in the more dilute acid solutions.

Plutonium(IV) forms a very insoluble, amorphous, olive-green hydroxide (see Table III-8 for its solubility in solutions of various anions). Plutonium(IV) also has a tendency to form a bright green solution containing various sized aggregates, at least part of which have been found to be of colloidal dimensions. These solutions are at present believed to be analogous to solutions of "meta ceric oxide", $Ce_{24}O_{15}(OH)_{60}(OH)_6$. The phenomenon of dispersion of the "hydroxide"

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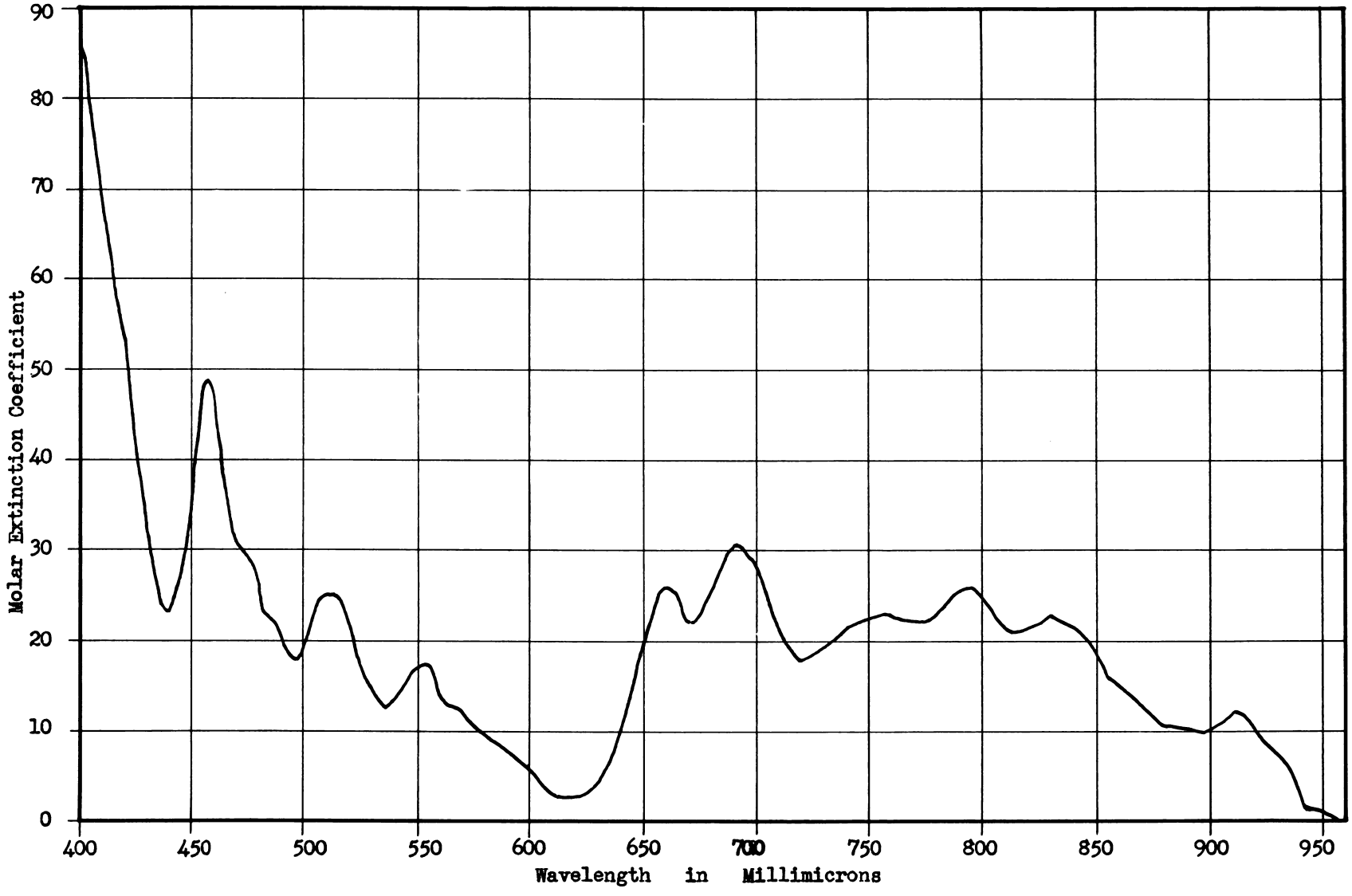

Fig. III-15. Absorption Spectrum of Complexes of Pu(IV) with Acetate

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into particles of colloidal size is widely observed among the (IV) ions (for example, Th(IV), U(IV), Ce(IV), etc.). Plutonium(IV) may be prepared in this form in at least two ways: (1) by warming dilute acid (0.1 to 0.3 molar) solutions of Pu(IV), and (2) by dispersing a well washed hydroxide with small quantities of acid. The plutonium in such solutions precipitates on addition of acid or much less than the stoichiometric amounts of ions such as oxalate or iodate. Conversion of Pu(IV) in the colloidal state to ionic solution is slow in dilute acid. Figures III-16 and III-17 illustrate the transformation from the bright green form of Pu(IV) to an ionic solution in 1 M HNO_3.

Ionic Species and Complexes of Pu(VI)

The absorption spectra of Pu(VI) in 1 M HNO_3 and 1 M $HClO_4$ shown in Figures III-18 and III-19 indicate that the ionic species present is the same in both solutions. There is spectrophotometric evidence for the formation of complex ions of Pu(VI) in both 1 M H_2SO_4 and 1 M HCl solutions. Some complex ion formation occurs in 9.4 M HNO_3 solutions of Pu(VI) as shown in Figure III-20.

Chloride Complexes.-- Absorption spectra measurements on solutions of Pu(VI) in HCl show an appreciable fraction of the PuO_2^{++} to be complexed at HCl concentrations as low as 0.5 molar. The wave length of the absorption bands characteristic of this complex are slightly longer than are the corresponding bands of the uncomplexed PuO_2^{++}. No value has as yet been obtained for the equilibrium constant, nor is the formula

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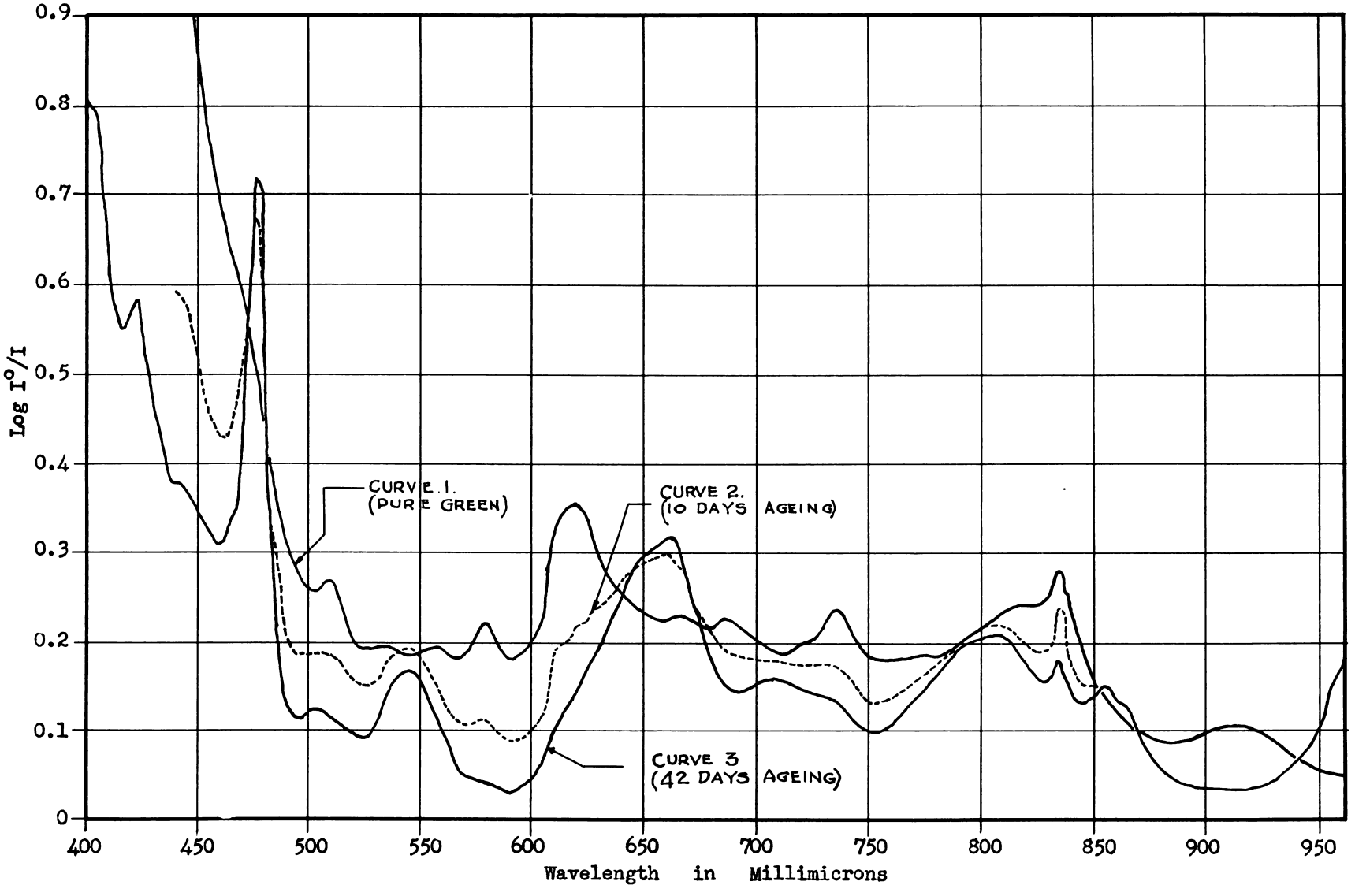

Fig. III-16. Transformation of Colloidal to Ionic Pu(IV) (A)

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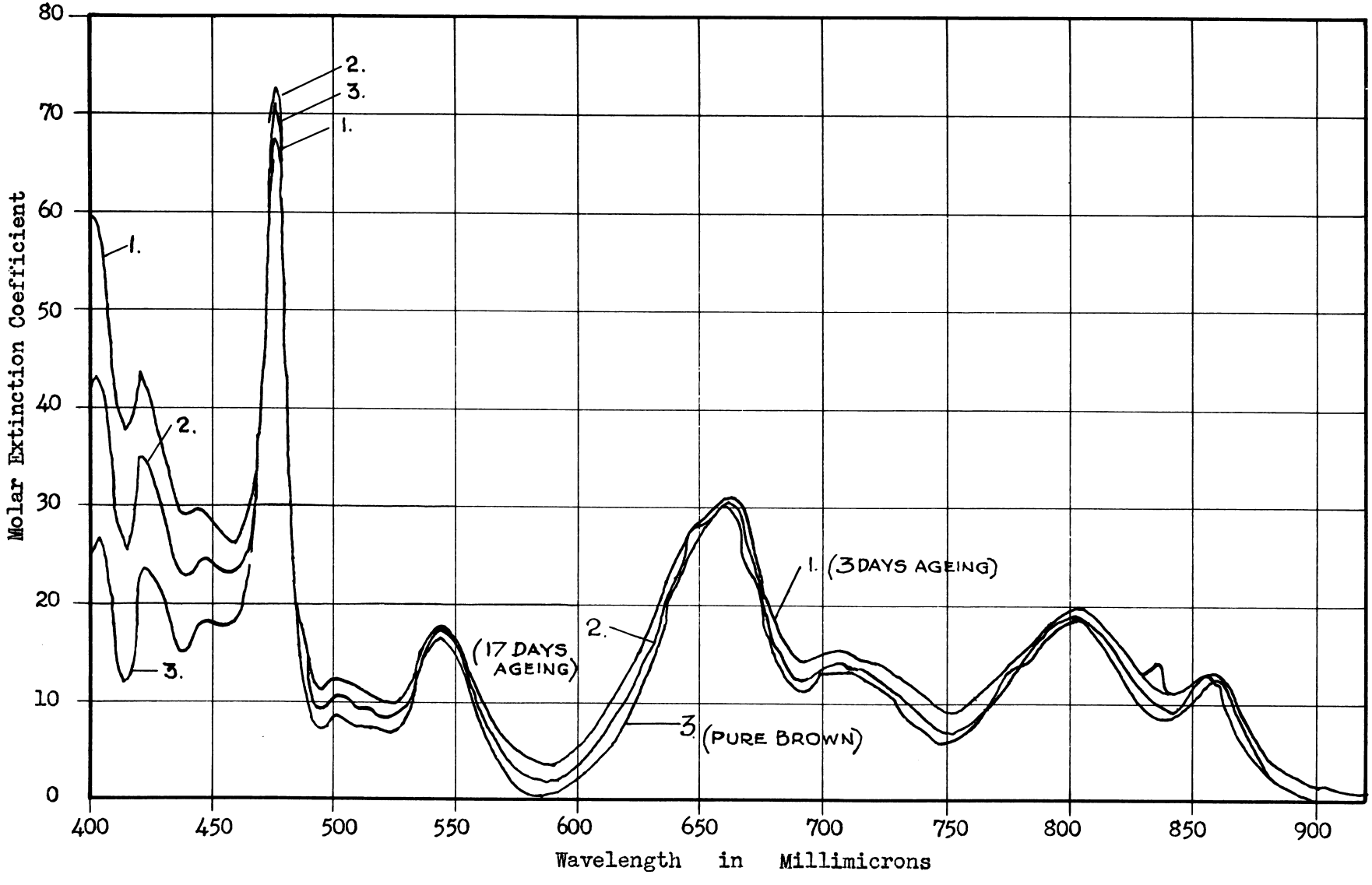

Fig. III-17. Transformation of Colloidal to Ionic Pu(IV) (B)

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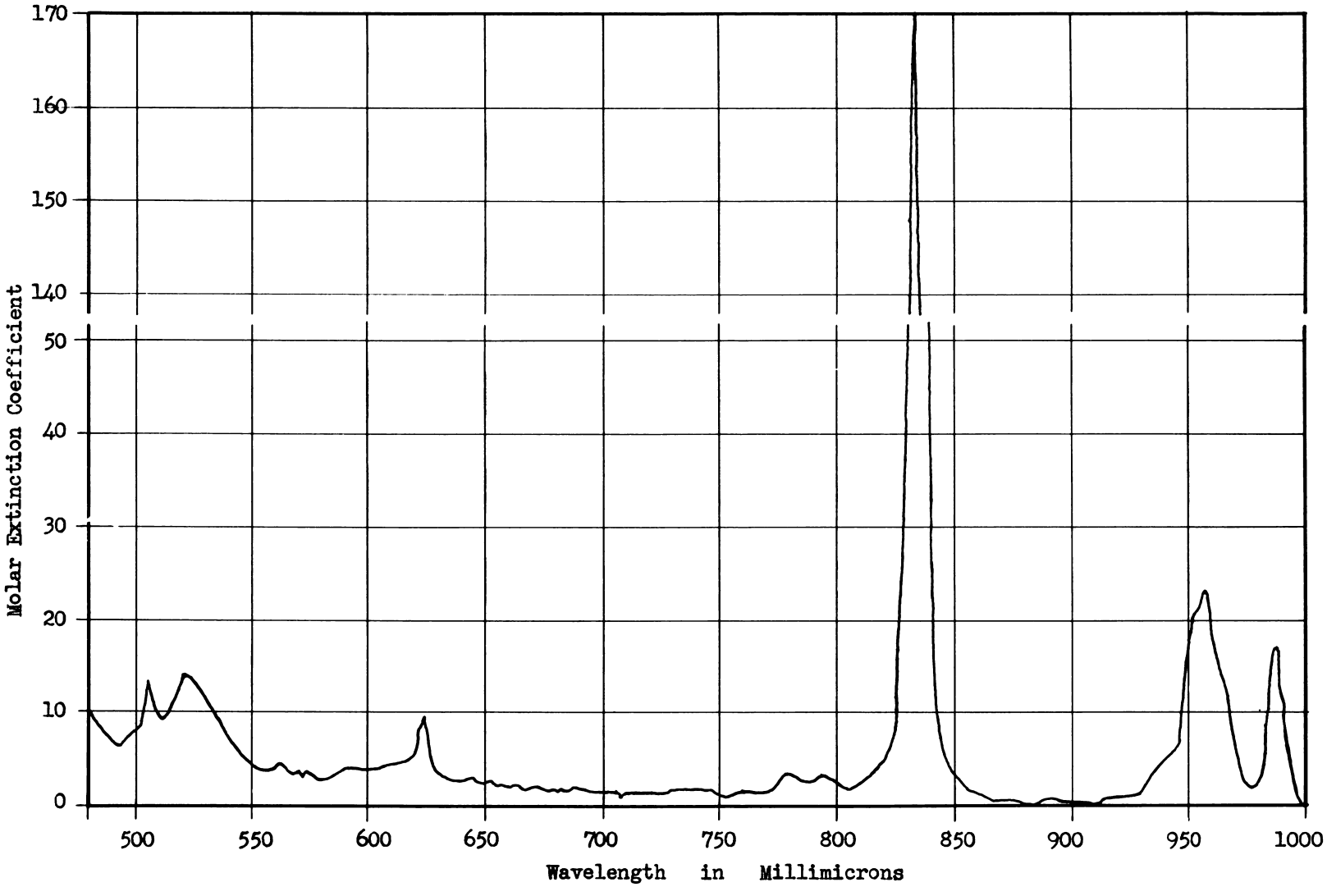

Fig. III-18. Absorption Spectrum of Pu(VI) in 1 M HNO_3

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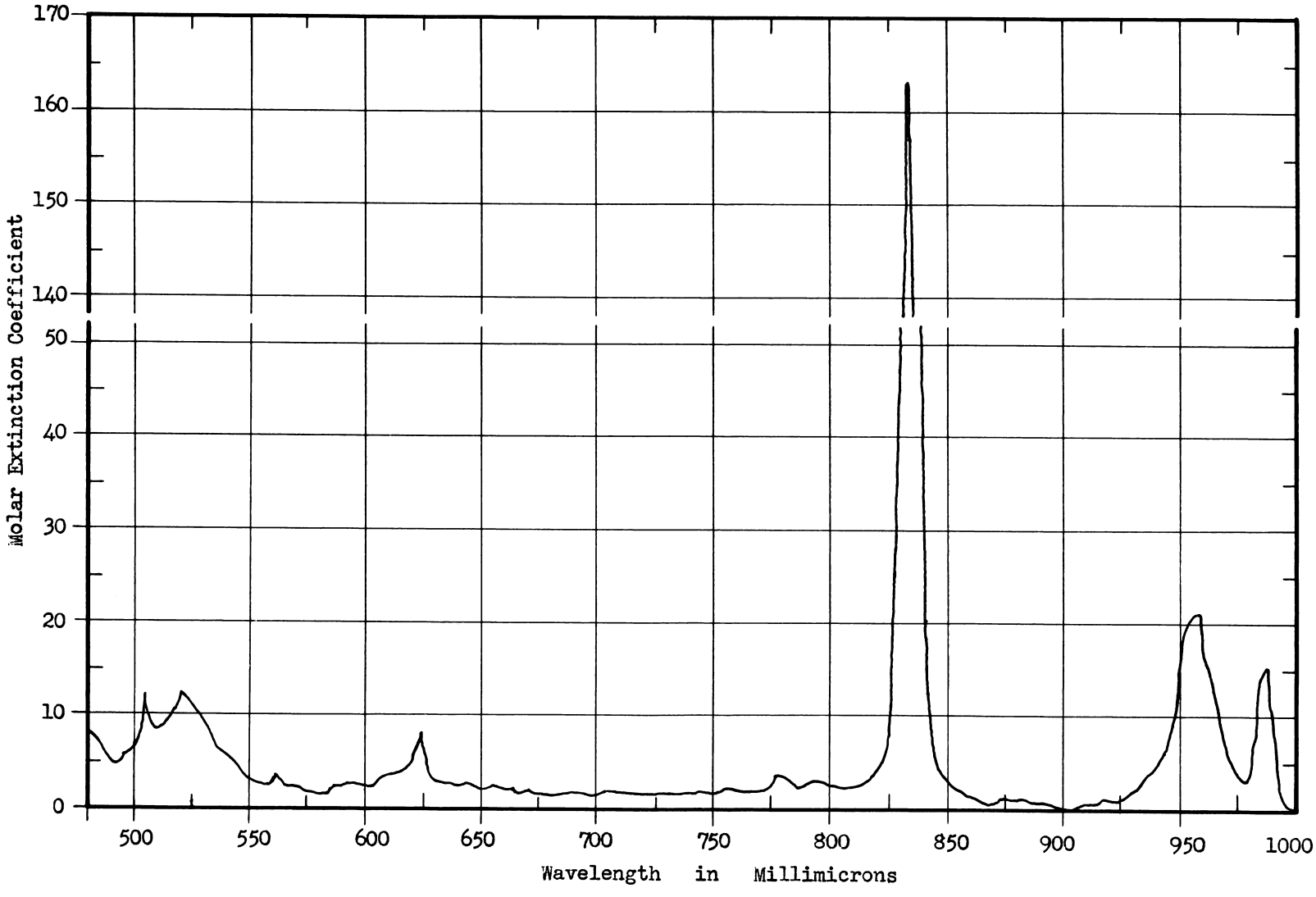

Fig. III-19. Absorption Spectrum of Pu(VI) in 1 M $HClO_4$

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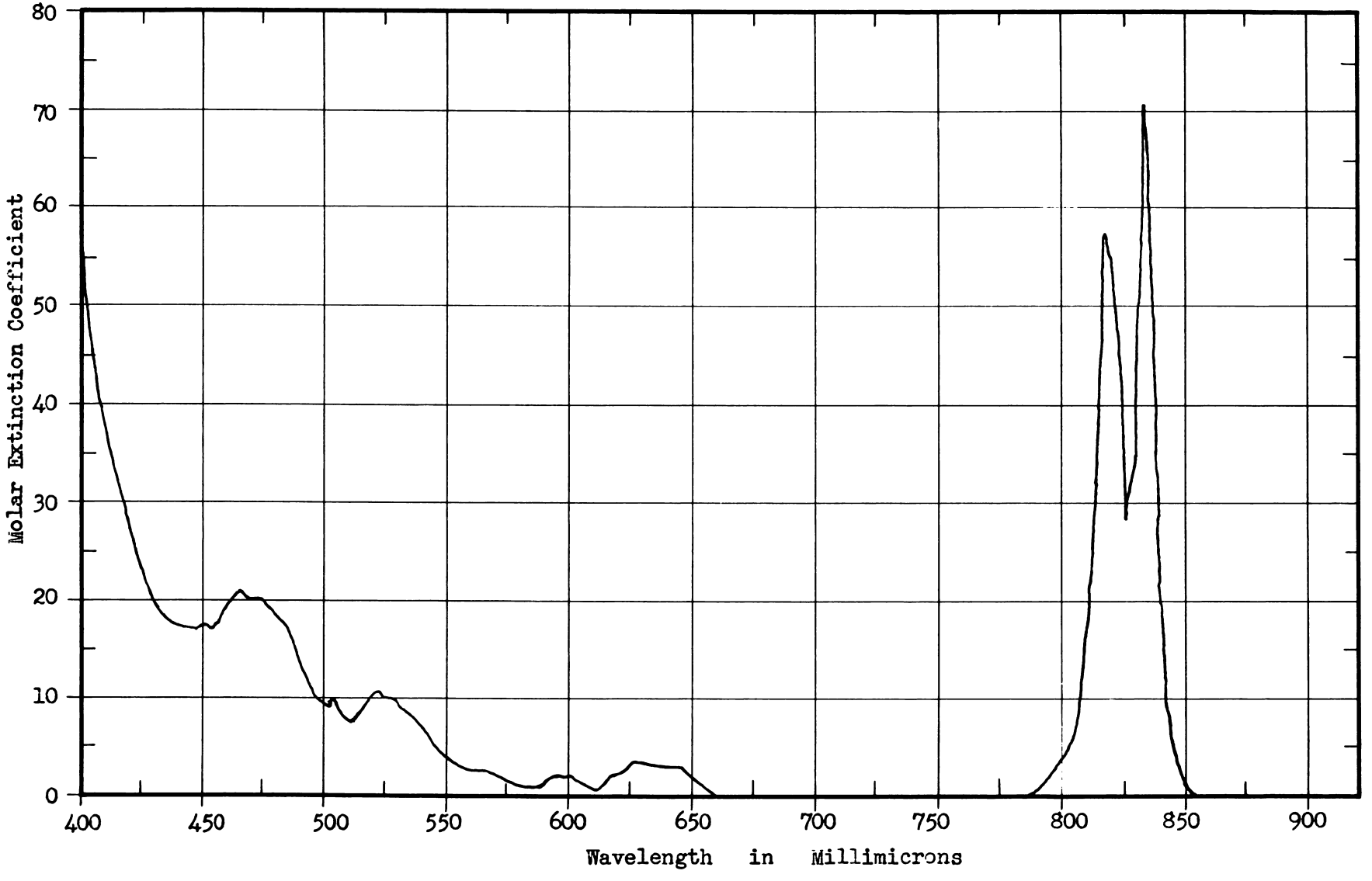

Fig. III-20. Absorption Spectrum of Pu(VI) in 9.4 M HNO_3

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of the complex known. Increasing the temperature of the Pu(VI) solution very markedly increases the proportion of the Pu(VI) present as the complexed form as demonstrated in Figure III-21. A similar increase in temperature when the Pu(VI) is in a 0.5 M HNO_3 solution has little influence on the absorption spectrum.

The Plutonyl Ion.-- By analogy with uranium it has been proposed that the PuO_2^{++} ion exists in acid solutions of Pu(VI). It has been experimentally indicated that the potentials of the Pu(III), Pu(VI) and Pu(IV), Pu(VI) couples appear to have a fourth power hydrogen ion concentration dependence, in conformity with the equations:

$$Pu^{+3} + 2\ H_2O = PuO_2^{++} + 4\ H^+ + 3\ e^-$$

$$Pu^{+4} + 2\ H_2O = PuO_2^{++} + 4\ H^+ + 2\ e^-$$

The postulate of the existence of PuO_2^{++} is supported by a great mass of chemical data showing the similarity in the behavior of U(VI) and Pu(VI). The (VI) state in alkaline solution is believed to be either a plutonate or polyplutonate analogous to U(VI) in alkaline solution.

Acidity of Pu(VI).-- In contrast to U(VI), Pu(VI) does not readily precipitate a hydroxide when its solutions are made slightly basic. Only the plutonate, or polyplutonate double salts appear upon making Pu(VI) solution basic with sodium hydroxide. These compounds precipitate much more slowly than do the uranates and polyuranates. They seem to be more soluble than U(VI) compounds formed under similar conditions in basic solution.

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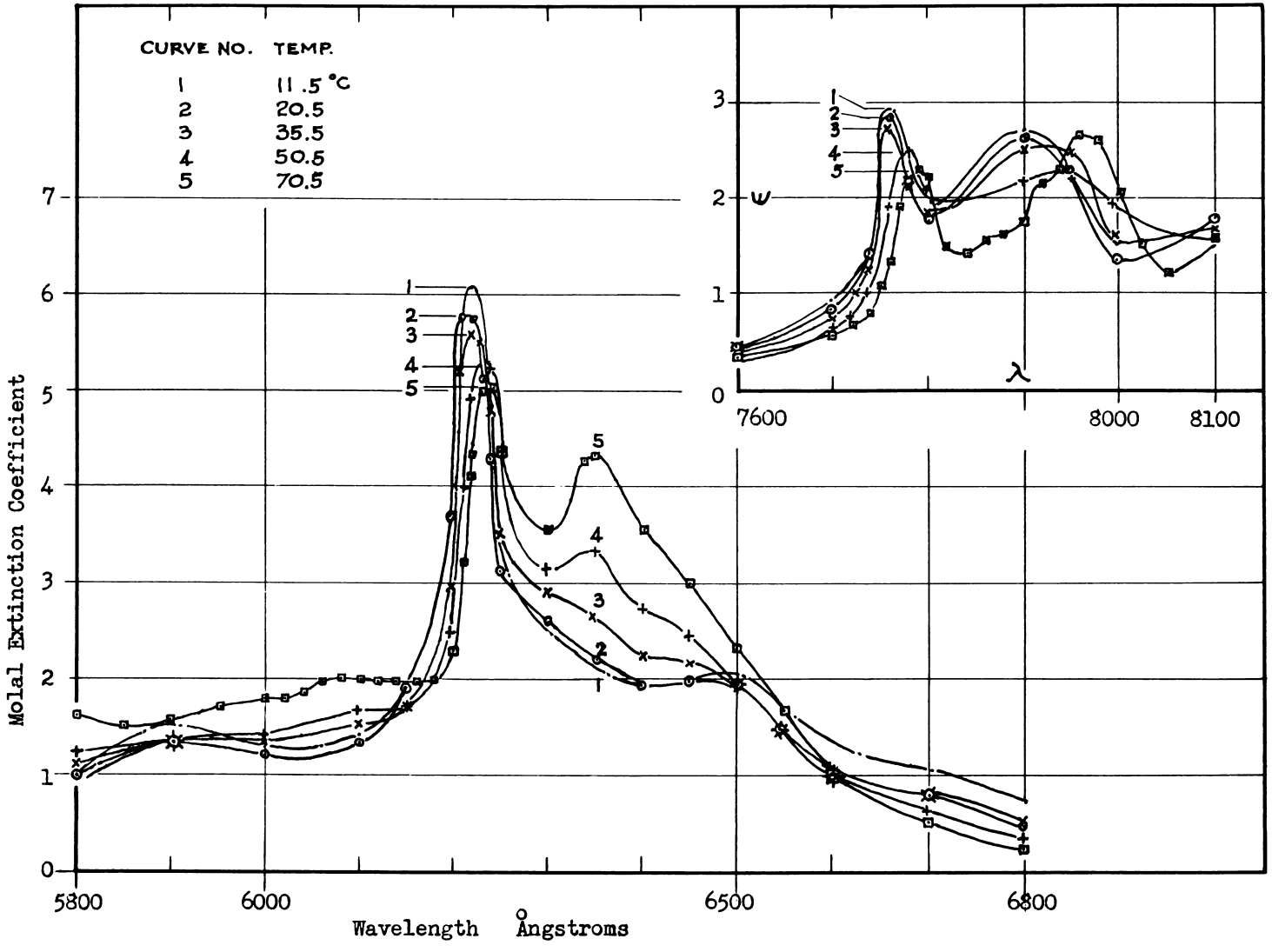

Fig. III-21. Effect of Temperature on Absorption Spectrum of Pu(VI) in 0.5 M HCl

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Curves, relating the pH to the equivalents of alkali added to solutions of Pu(VI), show an inflection point after two equivalents of base have been added. If the existence of the PuO_2^{++} ion is postulated, the reaction would correspond to:

$$PuO_2^{++} + 2\ OH^- = PuO_2(OH)_2$$

In contrast to UO_2^{++} solution, no immediate precipitation is observed. A precipitate does settle out, however, on standing a few days. The situation is probably more complicated since similar experiments on UO_2^{++} have indicated that more than one solid phase can be formed, for example:

$$UO_2^{++} + 2\ OH^- = UO_2(OH)_2$$

$$2UO_2^{++} + 6\ OH^- + 2\ Na^+ = Na_2U_2O_7 + 3\ H_2O$$

SOLUBILITY OF PLUTONIUM COMPOUNDS

In this section solubility data on various compounds of plutonium have been collected. No attempt has been made to include all the available data but only to collect those data useful in the discussion of ionic species and complex formation contained in the preceding section, and those which show the solubility of plutonium compounds in solutions of general rather than limited interest.

Solubility Data

Sources of Error.-- Solubility data have been obtained by radiochemical assay of the plutonium present in an aqueous phase which is in equilibrium with the plutonium compounds of interest. The most obvious

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sources of error are: (1) inaccurate radiochemical assays which can be eliminated by very careful technique; (2) the existence of plutonium in a highly dispersed state which makes its separation from the supernatant impossible; and (3) failure to establish true equilibrium which can be detected if solubility equilibrium is approached from both directions, or if measurements made over a long period of time show constant solubility values.

In addition to the above more obvious sources of error, two other uncertainties in the evaluation of the data should be pointed out. Solubility measurements on plutonium compounds are subject to errors of a type uncommon to solubility work in general, in that the oxidation states of plutonium are separated by such small energy differences and are so readily stabilized relative to each other by complex ion formation that it is frequently difficult to maintain a single desired oxidation state in solution. This applies particularly to the (III) and (VI) oxidation states. During the course of the measurements reported in this section, reasonable precautions were taken to reduce the errors from this source to a negligible magnitude, but in some cases proof that this was accomplished cannot be given.

In many cases the formulae of the solid phases are given. With some exceptions, which are noted, the identification of the solid phases was accomplished by X-ray diffraction analyses. In general, however, for a given precipitant the solid phase resulting from but one of a set of solubility conditions was identified. It is probable, but not certain, that the same solid phase was present under all solubility

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conditions employing a given precipitant. An obvious possibility, however, is that measurements made at pH greater than unity may in some cases be representative of basic rather than normal salts.

Arrangement and Reliability of Data.-- All the solubility data are contained in Table III-8 which is divided into three sections according to the oxidation state of plutonium in the compounds considered. Within each division the compounds are arranged alphabetically.

Solubility data marked with an asterisk (*) are estimated to be reliable to ± 10 per cent and are the results of determinations made under conditions of continuous agitation of the solid and liquid phases where constancy of the solubility data with time indicated that equilibrium had been established. The other data are either approximate or were obtained under conditions not clearly defined and, while some of them may be reliable, others may be in error by factors of 2 to 5. Unless otherwise noted, the temperature of the measurements may be taken as $25^{\circ} \pm 2^{\circ}C$.

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Table III-8. Solubilities of Plutonium Compounds

A. COMPOUNDS OF Pu(III)

Solid Phase	Aqueous Phase	Solubility in mg Pu/l.	Remarks
Fluoride $PuF_3 \cdot xH_2O$	1 M HF-0.25 M HCl	69*	Purple-isomorphism with $LaF_3 \cdot xH_2O$ indicated by X-ray diffraction studies.
	" -0.50 "	49*	
	" -1.0 "	37*	
Hydroxide $Pu_2O_3 \cdot xH_2O$	5 M NH_4OH	90	Blue-amorphous - readily susceptible to air oxidation.
Oxalate $Pu_2(C_2O_4)_3 \cdot xH_2O$	3.7 M H^+-0.5 M $H_2C_2O_4$	460	Acid anion not specified.
	1.96 " -0.2 "	290	
	0.75 " -0.2 "	21	
	0.22 " -0.14 "	6	
Phosphate $PuPO_4$	0.6 M H_3PO_4-0.15 M HNO_3	7*	Purple hexagonal crystalline phosphate isomorphous with both $BiPO_4$ and $CePO_4$.
	0.6 " -0.25 "	8*	
	0.6 " -0.53 "	20*	
	0.6 " -1.0 "	28*	
	0.8 M H_3PO_4-0.1 M HCl	20*	Structure identified by X-ray diffraction method.
	" -0.25 "	66*	
	" -0.50 "	210*	
	" -0.90 "	3890*	
	0.8 M H_3PO_4-0.08 M H_2SO_4	32*	
	" -0.23 "	37*	
	" -0.49 "	199*	
	" -0.98 "	545*	
	0.8 M H_3PO_4-0.1 M H_2SO_4	23*	Measurements carried out at 75°C.
	" -0.3 "	120*	
	" -0.4 "	900*	

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Table III-8, Continued.

B. COMPOUNDS OF Pu(IV)

Solid Phase	Aqueous Phase	Solubility in mg Pu/l.	Remarks
Bromate $Pu(BrO_3)_4$	1.5 M H_2SO_4-0.15 M $KBrO_3$	> 8000	
Carbonate (?)	1.0 M Na_2CO_3	72	Not certain whether a carbonate or a hydroxide precipitates.
	2.5 "	140	
Ferrocyanide (?)	6 N HCl	10-15	Reduction to Pu(III) and oxidation to ferricyanide may have occurred.
Fluoride $PuF_4 \cdot xH_2O$	0.1-2.0 M HNO_3 + 0.5-2.0 M HF	350-700*	
2 $LaF_3 \cdot PuF_4$ (?)	0.5-2.0 M HNO_3 + 0.5-2.0 M HF	20-70*	Some chemical evidence but no crystallographic evidence for the existence of this compound.
$K_2PuF_6 \cdot H_2O$	0.5-2.0 M HNO_3 + 0.5-2.0 M HF	10-50*	Isomorphous with $K_2CeF_6 \cdot H_2O$ and $K_2ThF_6 \cdot H_2O$
"Hydroxide" $PuO_2 \cdot xH_2O$	0.01 M Na_2SO_4	pH + log solubility = 3.4, over pH range 3.0-4.30.	2-5 day equilibration period.
	0.01 M Na_2SO_4	pH + log solubility = 6.0, over pH range 2.50-2.90.	2-5 day equilibration period.
	0.01 M Na_2SO_4 pH = 5.40	0.018*	2-5 day equilibration period.
	0.341 M Na_2SO_4 pH = 2.11	409*	Yellow brown solid phase. 29 day equilibration period.
	0.406 M Na_2SO_4 pH = 3.09	30*	

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Table III-8 - B. COMPOUNDS OF Pu(IV) - Continued

Solid Phase	Aqueous Phase		Solubility in mg Pu/l.		Remarks
	0.333 M Na_2SO_4	pH = 3.88	4.7*		Greenish brown solid phase. 29 day equilibration period.
	0.333M Na_2SO_4	pH = 4.25	2.9*		Light green solid phase. 29 day equilibration period.
"Hydroxide" $PuO_2 \cdot xH_2O$	0.1 M $NaClO_4$		pH + log solubility = 2.11, over pH range 2.60-3.25		
	0.1 M $NaClO_4$		Solubility independent of pH over pH range 4.13-5.02		
	1.0 M Na_2SO_4	pH = 1.91	2390*	15 day equilibration period.	
	"	2.23	860*	8 "	" "
	"	2.69	274*	7 "	" "
	"	3.21	355*	6 "	" "
	"	3.60	300*	6 "	" "
	"	4.15	217*	2 "	" "
	"	4.17	71*	6 "	" "
	"	5.09	16*	2 "	" "
	"	6.25	1.11*	6 "	" "
	"	2.44	204*	27 "	" "
	"	2.80	66*	27 "	" "
	"	3.15	65*	27 "	" "
	"	3.35	16*	24 "	" "
	"	3.64	48*	24 "	" "
	"	3.90	111*	24 "	" "
	"	6.2	5.9*	22 "	" "

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Table III-8 - B. COMPOUNDS OF Pu(IV) - Continued

Solid Phase	Aqueous Phase	Solubility in mg Pu/l.	Remarks
Iodate $Pu(IO_3)_4$	0.1 M KIO_3-1.0 M HNO_3	3.7*	Pale tan, amorphous compound. Composition determined by chemical analysis.
	" -2.0 "	5.4*	
	" -3.0 "	6.6*	
	" -4.0 "	13.7*	
	" -5.0 "	46.5*	
	" -6.0 "	94.5*	
	0.15 M KIO_3-1.0 M HNO_3	1.6*	
	" -2.0 "	2.1*	
	" -3.0 "	2.5*	
	" -4.0 "	6.9*	
	" -5.0	16.5*	
	" -6.0 "	24.9*	
Molybdate	Excess MoO_4^{--} at pH = 2	16	Microgram scale 0.5 hour equilibration.
	" pH = 4	17	
Oxalate $Pu(C_2O_4)_2 \cdot 6H_2O$	0.05 M $H_2C_2O_4$-0.1 M HNO_3	32*	Green crystalline compounds, isomorphous with $U(C_2O_4)_2 \cdot 6H_2O$ and $Th(C_2O_4)_2 \cdot 6H_2O$. Composition determined by both crystallographic and chemical methods.
	" -0.5 "	15*	
	" -1.0 "	11*	
	" -2.0 "	15*	
	0.10 M $H_2C_2O_4$-0.1 M HNO_3	175*	
	" -0.5 "	48*	
	" -1.0 "	25*	
	" -2.0 "	14*	
	" -4.0 "	26*	
	" -6.0 "	49*	

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Table III-8 - B. COMPOUNDS OF Pu(IV) - Continued

Solid Phase	Aqueous Phase	Solubility in mg Pu/l.	Remarks
Nitrate $Pu(NO_3)_4 \cdot xH_2O$	2 N HNO_3	500×10^3	Approximate value.
$Pu(C_2O_4)_2 \cdot 6H_2O$	0.75 M HNO_3 + $H_2C_2O_4$	$[\text{Solubility}] = 7.5 + 277\,[H_2C_2O_4]$. (Table III-6) Accurate to $\pm$ 3% in the range 0.4 to 0.018 M $H_2C_2O_4$.	
$Pu(C_2O_4)_2 \cdot 6H_2O$	0.2 M $H_2C_2O_4$-0.1 M HNO_3	150*	-
	" -0.5 "	94*	
	" -1.0 "	53*	
	" -2.0 "	30*	
	1 M HNO_3-0.5 M HF-0.1 M $H_2C_2O_4$	75*	
	" -1.0 " -0.1 "	>244*	
Peroxide $PuO_4 \cdot xH_2O$ (?)	1 M HNO_3-0.6 % H_2O_2	710*	Composition determined by chemical analysis.
	" -2.5 "	60*	
	" -5.0 "	70*	
	" -5.4 "	50*	
	" -7.5 "	20*	
	" -10.0 "	20*	

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Table III-8 - B. COMPOUNDS OF Pu(IV) - Continued

Solid Phase	Aqueous Phase	Solubility in mg Pu/l.	Remarks
Phosphate $Pu_3(PO_4)_4 \cdot xH_2O$ (?)	0.1 M H_3PO_4-0.1 M HNO_3	0.13*	
	" -0.5 "	1.7*	
	" -1.0 "	4.5*	
	" -2.0 "	23.0*	
	0.6 M H_3PO_4-0.1 M HNO_3	3.7*	
	" -0.5 "	7.9*	
	" -1.0 "	19.0*	
	" -2.0 "	77.0*	
	0.1 M H_3PO_4-0.1 M H_2SO_4	4*	
	" -0.5 "	63*	
	" -1.0 "	550*	
	0.8 M H_3PO_4-0.1 M H_2SO_4	18*	Isomorphous with $Th_3(PO_4)_4 \cdot xH_2O$ and $Ce_3(PO_4)_4 \cdot xH_2O$.
	" -0.5 "	81*	
	" -1.0 "	120*	
	" -2.0 "	563*	
	0.8 M H_3PO_4-0.1 M H_2SO_4	24* (75°C.)	
	" -0.25 "	36* "	
	" -0.50 "	80* "	
	" -1.0 "	290* "	
	0.6 M H_3PO_4-0.1 M HCl	4*	
	" -1.0 "	12*	
	0.8 M H_3PO_4-0.1 M HCl	12*	
	" -0.5 "	16*	
	" -1.0 "	29*	
	" -2.0 "	72*	

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Table III-8, Continued.

C. COMPOUNDS OF Pu(VI)

Solid Phase	Aqueous Phase	Solubility in mg Pu/l.	Remarks
Chloride $PuO_2Cl_2 \cdot xH_2O$	~5 M HCl	350×10^3	
Nitrate $PuO_2(NO_3)_2 \cdot xH_2O$	~0.5 M HNO_3	500×10^3	Orange, hygroscopic needles.
Sodium Plutonyl Acetate $NaPuO_2Ac_3$	0.6 M HAc-0.2 M NaAc-0.3 M $NaNO_3$	1000	Pink crystalline compound, crystallizing in tetrahedra. Isomorphous with $NaUO_2Ac_3$.
	" -0.2 " -2.1 "	280	
	" -0.2 " -4.0 "	170	
	" -0.2 " -5.7 "	70	
	H_2O	6.1×10^3 5° C.	
		9.6×10^3 25°C.	
		11.1×10^3 55°C.	
		18.7×10^3 95°C.	
Hydroxide (?) Ammonium Plutonate (?)	3 M NH_4OH (carbonate free)	1000	

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Qualitative Data on Organic Precipitants for Plutonium.-- The principal interest in organic reagents was their use in the formation of extractable organic plutonium complexes as a method of purification (Chapter V). However, a limited investigation of the use of organic precipitants for plutonium was carried out.

Most of the available data were obtained during the early work on a microgram scale and the solid phases could not be identified. It was also difficult on this scale to clearly define the conditions of precipitation. As a result, it is believed that the data which are reported in Table III-9 should be considered from a qualitative point of view.

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Table III-9. Qualitative Data on Organic Precipitants for Plutonium

Precipitant	Appearance of Precipitate	Order of Solubility	Remarks
Benzoic Acid	White amorphous precipitate with Pu(III) and Pu(IV)	"Very soluble"	Conditions unknown.
Cinnamic Acid	Pale green amorphous precipitate with Pu(IV)	60 mg/l. at pH 4-5	
Fumaric Acid	Olive green amorphous precipitate with Pu(IV)	25 mg/l. at pH = 4	Precipitate soluble in $CHCl_3$ (?)
8-Hydroxyquinoline	Dark red crystals with Pu(IV)	77 mg/l; pH = 4 17 mg/l; pH = 8	Precipitate is $Pu(C_9H_7ON)_4$. Is soluble in $CHCl_3$.
m-Nitrobenzoic Acid	White amorphous precipitate with Pu(IV)	4 mg/l; at pH = 5	
Phenylarsonic Acid	White crystalline ppt. with Pu(IV) and no precipitate with Pu(III)	"Insoluble"	Conditions unknown.
Picrolonic Acid	Apple green crystalline ppt. of Pu(III) Pink crystalline ppt. of Pu(IV)	Pu(III)-90 mg/l.	
Salicylic Acid	White crystalline (?) ppt. with Pu(IV)	"Insoluble"	PPt. soluble in C_6H_6 (?)

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THE OXIDES, HALIDES AND OXYHALIDES OF PLUTONIUM

In aqueous solution the oxidation states (III), (IV), (V) and (VI) are observed for plutonium. Here the higher states are stabilized by solvation and complex ion formation. In solid compounds the small positively charged plutonium ions of the higher oxidation states must be stabilized by coordination to the anions of strongly electronegative atoms such as O^- or F^-. No simple oxide of the (V) or (VI) state is known. In solid compounds of the Pu(VI) state, such as $NaPuO_2(C_2H_3O_2)_3$, the Pu(VI) is highly coordinated to oxygen anions. Plutonium(V) or Pu(VI) exists as a fluoride or oxyfluoride in the "higher fluoride of plutonium". Plutonium(IV) exists as a fluoride and oxide and probably not as any other halide (although oxyhalides may be stable); Pu(III) exists as any of the halides or oxyhalides and probably as the oxide.

Plutonium Oxides

The known oxides of plutonium are PuO_2, "Pu_2O_3", and PuO. In addition to these compounds, hydrous oxides of Pu(III), Pu(IV) and possibly Pu(VI) may be precipitated from aqueous solution as can the peroxide of Pu(IV).

Plutonium Dioxide.-- The dioxide, PuO_2, is the most stable oxide of plutonium and it is the end product of the ignition in air of most plutonium compounds. Its composition has been established by chemical analysis and by X-ray analysis. It is commonly prepared by igniting the following compounds in air in the temperature ranges listed:

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$Pu(NO_3)_4 \cdot xH_2O$ at 300° to 1000°C.; $PuO_2(NO_3)_2 \cdot xH_2O$ at 230° to 1000°C. and $Pu_2(C_2O_4)_3$ at 300° to 1000°C.

The dioxide, when pure, generally is yellow-green in color. It has been observed that the dioxide undergoes color changes as it cools from 1000°C. to room temperature. Plutonium(IV) hydroxide ($PuO_2 \cdot xH_2O$), air dried at 70°C., contains PuO_2 crystallites of about 30 Å in linear dimensions according to X-ray diffraction data. It also contains some water. When this substance is ignited in air to 700°C., the PuO_2 obtained is black in color.

A finely divided form of oxide, such as $PuO_2 \cdot xH_2O$ or the oxide obtained by ignition of the nitrate at a relatively low temperature (300°C.), is most suitable for conversion of oxide to a halide. The oxide ignited at 700° to 1000°C. is very refractory and dissolves with difficulty in fuming H_2SO_4 or $HClO_4$; fusion with Na_2CO_3 or $Na_2S_2O_7$ is more effective.

Plutonium "Sesquioxide".— The phase "Pu_2O_3" has been characterized only by its X-ray pattern and its probable formula based only on crystal chemical considerations corresponds to an O/Pu atom ratio lying between 1.5 and 1.75.

Among the products obtained by an attempted atomic hydrogen reduction of PuF_3 the phase "Pu_2O_3" was identified by X-ray diffraction observations along with some PuN and PuO_2. The various products arise presumably due to impurities in the atomic hydrogen system.

After heating a pellet of PuO_2 on a tantalum filament in vacuo to 1800°C., the compound "Pu_2O_3" was identified in the residue. The color

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of the PuO_2 changed from yellcw to black at 1100°C., and at 1700° to 1800°C. the substance melted and acquired a metallic appearance. It is not certain whether this decomposition represents a reduction by the tantalum of the filament or whether it is a thermal decomposition in which O_2 gas is evolved from the PuO_2.

In vapor phase reductions of PuO_2 with Ba, some "Pu_2O_3" was formed, along with considerable unreacted PuO_2.

In some attempts to make Pu carbide by firing a mixture of PuO_2 and graphite, some "Pu_2O_3" was formed.

Various other attempts to make "Pu_2O_3" have failed; PuO_2 treated with H_2 at 1000°C. in a porcelain vessel is not reduced to "Pu_2O_3". When PuO_2 is treated with H_2 at 1000° to 1200°C. in a platinum vessel, there is a loss in weight which is attributed to the formation of a Pt-Pu alloy containing about 1 per cent by weight Pu; the reduction to metal proceeding because of the decrease in free energy accompanying the alloy formation. The oxide phase in contact with the alloy of platinum and plutonium remains PuO_2. This presumably means that Pu_2O_3 is unstable when in contact with platinum above 1000°C., disproportionating to give PuO_2 and a platinum-plutonium alloy or compound. Vacuum drying of a plutonium(III) hydroxide precipitate gave rise to only a PuO_2 crystalline phase. Thermal decomposition of $Pu_2(C_2O_4)_3$ in H_2 or CO_2 at one atmosphere pressure gave rise to PuO_2 above 300°C. (identified by X-ray analysis and the weight change).

Since heating $PuCl_3 \cdot 6H_2O$ in a sealed tube in vacuo to 600°C. gives rise to a mixture of PuOCl and PuO_2, it is clear that Pu_2O_3 readily reduces H_2O to give PuO_2 and H_2.

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Plutonium Monoxide.-- This substance has been obtained by the reduction of PuOCl with Ba vapor at 1250°C. It was also frequently obtained as one of the products in attempted reductions of PuF_3 with Li or Ba vapor on the microscale (less than 1 mg.) in systems that were not subjected to a thorough degassing.

Plutonium monoxide has appeared as a black, cokey mass or as a material showing metallic reflections. It is more brittle and less malleable than is Pu metal. It readily dissolves in aqueous HCl with the liberation of H_2.

The observations and studies of PuO have been made with too small quantities of material to permit reliable conclusions as to the type of binding in this compound. Since the known oxidation states in aqueous solution are (III), (IV), (V) and (VI), it seems probable that the binding in PuO has some metallic character. It is not permissible to infer this, however, from the metallic appearance of PuO samples, since "Pu_2O_3" samples may also have this appearance.

Higher Oxides.-- There are no known higher oxides of plutonium corresponding to possible formulae Pu_2O_5, Pu_3O_8, or PuO_3.

Controlled ignition of $PuO_2 \cdot (NO_3)_2 \cdot xH_2O$ in dry air gave no gravimetric evidence for the existence of a higher oxide of plutonium. There was only gradual decomposition producing PuO_2 above 230°C.

Potentiometric titrations (glass electrode) of a $PuO_2(NO_3)_2$ solution with NaOH indicate that a $PuO_3 \cdot xH_2O$ may be precipitated from solution.

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Plutonium Peroxide.-- There is evidence that Pu in plutonium peroxide is in the Pu(IV) state and that the compound contains between 3 and 4 peroxide oxygens per Pu atom. Solubility data are given in Table III-8.

Plutonium Halides and Oxyhalides

The known fluoride compounds of plutonium are PuF_3, PuF_4, K_2PuF_6, PuOF, $PuOF_2$(?) and the "higher fluoride" whose composition probably corresponds to one of the formulae PuF_6, PuF_5, $PuOF_4$ or $PuOF_3$.

The other halogens all form the compounds PuX_3 and PuOX. There is no evidence for the formation of PuX_4 in these cases and it is probable that these compounds are unstable with respect to decomposition into PuX_3 and X_2 even at room temperature.

Fluoride Compounds.--

1. PuF_3. Plutonium trifluoride has been identified by chemical analysis and crystallographic considerations. It is conveniently prepared by various methods and is ordinarily obtained as a purple product although occasionally black preparations have been identified as PuF_3.

Ignited or hydrated PuO_2, $Pu(NO_3)_4$, $PuO_2(NO_3)_2$, $Pu(C_2O_4)_2$ or $Pu_2(C_2O_4)_3$ may be reacted with a mixture of HF and H_2 at 550° to 600°C. to yield PuF_3. About one per cent H_2 in the HF is sufficient to prevent conversion of the compounds listed, except $Pu_2(C_2O_4)_3$, to PuF_4 and tank HF usually contains enough H_2 in these cases to produce PuF_3 directly. Conversion of $Pu_2(C_2O_4)_3$ to PuF_3 is the method preferred at present.

The addition of HF to Pu(III) solutions precipitates PuF_3 which may be dried in a stream of HF at 300°C. to yield anhydrous PuF_3.

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Plutonium trifluoride may be taken into solution with Ce(IV) in the cold, or by fuming with sulfuric acid. Fluorine converts PuF_3 to PuF_4 at 200°C. When heated in moist O_2 or laboratory air to above 300°C., PuF_3 is converted to PuO_2. PuF_3 reacts with dry oxygen at an atmosphere pressure at 600°C., according to yield PuF_4 and PuO_2 in the ratio 3:1. This reaction is readily reversed by pumping on the PuF_4,PuO_2 mixture at 600°C. for one hour. When treated with an O_2,HF mixture (80 per cent HF) at 600°C., it is converted to PuF_4 according to the equation:

$$PuF_3 + 1/4\ O_2 + HF = PuF_4 + 1/2\ H_2O$$

Solubility data are given in Table III-8, and data on the vapor pressure and melting point are given in Table III-12.

2. PuOF. The compound PuOF has been obtained as one of the products of an attempted atomic hydrogen reduction of PuF_4 and by heating a sample of PuF_3 on a filament to 1600°C. in an argon atmosphere. In both of these preparations there was presumably an oxygen bearing impurity in the system. The identification of this compound depends on both X-ray considerations and chemical analysis.

3. PuF_4. The tetrafluoride may be prepared by the following methods:

(a) $PuO_2 + 4\ HF \xrightarrow{500°C.} PuF_4 + 2\ H_2O$

Pure HF will convert PuO_2 to PuF_4, not PuF_3. Since there is frequently H_2 gas in tank HF, it is advisable to add some O_2 (5 to 10 per cent) to the HF stream to remove the H_2. With too much O_2, the rate of production of PuF_4 is unsatisfactory. Instead of ignited PuO_2, Pu(IV) nitrate or $PuO_2 \cdot xH_2O$ may be used.

(b) $Pu(NO_3)_4(aq.) + 4\ HF\ (aq.) = PuF_4 \cdot 2.5\ H_2O(s) + 4\ HNO_3$

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This precipitate has been identified by its isomorphism with the corresponding $UF_4 \cdot 2.5\ H_2O$. It may be dried in HF at 350°C. to give anhydrous PuF_4.

As mentioned above, when PuF_3 is treated with an O_2,HF mixture, PuF_4 is produced. When PuF_4 is heated to 900°C. in vacuo in a platinum crucible, PuF_3 is formed. It is believed that this is due to the reaction

$$PuF_4 = PuF_3 + 1/2\ F_2$$

occurring at a low pressure of F_2. An H_2,HF mixture containing only 0.6 per cent H_2 by volume will reduce PuF_4 to PuF_3 at 600°C. In moist air or oxygen at 325°C., PuF_4 is converted to PuO_2. Dry oxygen does not attack PuF_4 in the temperature range 300° to 600°C. Chemical analyses indicate that under certain circumstances PuF_4 may absorb HF.

Plutonium tetrafluoride is pale brown in color and may be taken into solution with hot concentrated H_2SO_4 or HNO_3. Its solubility is reported in Table III-8.

3. K_2PuF_6. The addition of HF to a solution containing Pu(IV) and potassium ions precipitates $K_2PuF_6 \cdot xH_2O$. The compound K_2PuF_6 was identified by crystallographic considerations after the precipitated material was dried in vacuo at room temperature. Solubility data for this compound are given in Table III-8.

4. $PuOF_2$ (?). The addition of fluosilicic acid to a Pu(IV) nitrate solution precipitated a compound which after vacuum drying showed an X-ray pattern indicating isomorphism with a uranium preparation believed to be UOF_2.

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5. Plutonium Higher Fluoride. Although a considerable amount of experimental work has been done on "the higher fluoride of plutonium" its chemical identity and its properties have not been established. The well established facts about the higher fluoride of plutonium are summarized in the following statements.

(a) When samples of PuF_4 or PuO_2 (1 to 5 mg.) are treated with F_2 at temperatures of 500°C. or higher, for one-half hour, most of the plutonium usually volatilizes away. This is clear evidence that there is a higher fluoride or oxyfluoride of plutonium, since PuF_4 in a stream of HF at the same temperature does not volatilize.

(b) When the plutonium higher fluoride is volatilized from PuO_2 or PuF_4 in a stream of F_2 at or above 500°C. in a copper or nickel tube and passed through lengths of tubing which are maintained at controlled temperatures, the plutonium condenses on the walls of the tubing mostly in the temperature range from 150° to 0°C.

An attempt to interpret these experiments in terms of deposition of PuF_6 solid or liquid in equilibrium with gaseous PuF_6 leads to a heat of vaporization of 3 to 5 kilocalories per mole which is unreasonably low.

(c) If the plutonium higher fluoride is volatilized in a stream of F_2 and its deposition product is condensed at low temperature (100° to -80°C.), it is found that this condensed material is not re-volatilized upon heating in F_2 to 200°C., but is partially re-volatilized, about 80 per cent in one-half hour, at 300°C.

Several hypotheses have been advanced to explain the data on the volatilization, condensation and re-volatilization of the higher fluoride

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in copper of nickel equipment:

(a) The plutonium higher fluoride is a rather nonvolatile substance with a sublimation temperature of 300° to 500°C. The condensation is primarily a true condensation to form a solid phase of the plutonium higher fluoride; however, equilibrium is not attained and the material deposits more gradually than would be expected for condensation of a saturated vapor.

(b) Some chemical interaction with the walls of the container is involved, such as reduction by the nickel or copper of the higher fluoride to PuF_4 or adsorption by the nickel fluoride or copper fluoride layers on the tubing to give an addition compound from which the plutonium has a low volatility.

(c) The heat of reaction to form plutonium higher fluoride vapor from solid PuF_4 and gaseous F_2 is negative. This is the case for the synthesis of UI_4 vapor from UI_3 solid and iodine vapor. When iodine vapor is passed over UI_3 at 500°C., UI_4 volatilizes and UI_3, not UI_4, is deposited further down the tube at 380° to 300°C.

It is clear that the most satisfactory method to distinguish between these hypotheses and to ascertain the chemical nature of the higher fluoride of plutonium is to work with larger quantities of material and isolate the condensed plutonium compound and determine its formula by chemical analysis. At present, the higher fluoride of plutonium can reasonably be expected to be one of the following: PuF_6, PuF_5, $PuOF_4$ of $PuOF_3$. Tank fluorine usually contains more than 1 per cent of O_2 and therefore the oxyfluorides cannot be excluded by the method of synthesis.

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One experiment has been performed which strongly supports the concept of a volatile PuF_6. A one milligram sample of PuF_4 was mounted on a Ni filament that could be heated electrically in a stream of F_2. The Pu volatilized and a white condensate formed on an adjacent liquid oxygen cooled surface. The unique feature of the apparatus was the fact that the plutonium higher fluoride contacted no material of construction at an intermediate temperature but was volatilized directly from the hot nickel filament to the glass surface at liquid oxygen temperature. When warmed in vacuo, the white condensate sublimed below room temperature into an adjacent U-tube maintained at liquid oxygen temperature. On warming, in this tube, some melting was observed suggesting attack on the glass. The sample was frozen, the U-tube removed from the apparatus and the condensate was observed to dissolve cleanly in zirconyl solution. This solution by spectrophotometric analysis contained greater than 80 per cent of the original amount of plutonium and it was all in the (VI) state. These observations suggest that the substance was PuF_6 but since the experiment has not been repeated the results cannot be regarded as certain.

Investigations of the volatilization of PuF_4 in a low pressure of F_2 activated by a glow discharge have been made. Whereas UF_4 is formed and volatilized almost instantly in a similar experiment, plutonium is only very slowly volatilized.

Chloride Compounds.—

1. $PuCl_3$. Plutonium trichloride may be synthesized by the following methods:

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(a) $Pu + 3/2\ Cl_2$(60 mm.) (450°C.) = $PuCl_3$

(b) $PuH_3 + 3\ HCl$(1 atm.) (400°C.) = $PuCl_3 + 3\ H_2$

(c) $PuO_2 + 1/2\ H_2 + 3\ HCl$ (600-700°C.) = $PuCl_3 + 2\ H_2O$

PuO_2 ignited at 1000°C. reacts more slowly than does PuO_2 ignited at 300°C.

(d) $Pu_2(C_2O_4)_3 \cdot 9H_2O + H_2 + HCl = 2\ PuCl_3 +$ {Unidentified volatile products}

This reaction is carried out by gradually heating from 50° to 600°C. and is the preferred method for the production of large quantities of plutonium chloride. The material obtained by methods (b), (c) and (d) is described as blue-green in color.

(e) When an aqueous solution of $PuCl_3$ is evaporated to dryness in HCl gas at room temperature, $PuCl_3 \cdot 6H_2O$ is obtained. Heating this compound slowly to 250°C. in a stream of HCl yields anhydrous $PuCl_3$. In this synthesis, it is important to dehydrate the $PuCl_3 \cdot 6H_2O$ that first crystallizes out to a lower hydrate at a temperature below its melting point of 95°C. Otherwise, some PuOCl forms and it is difficult to convert this entirely to $PuCl_3$.

The $PuCl_3$ solution is readily prepared by reducing a $PuCl_4$ solution with a reducing agent which is itself volatile and gives rise to a volatile oxidized product. Hydrogen iodide or NH_4I appear to be the most satisfactory for reducing agents but HCHO, NH_3OHCl or H_2S may be used. If NH_4I is used, the final temperature of heating should be about 350°C. in order to sublime away the NH_4Cl. The material obtained is a slate blue in color. It may be sintered in HCl at a higher temperature (650°C.) to obtain a more macrocrystalline material.

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(f) $PuO_2 + 2\ CCl_4$ (ca. 800°C.) $= PuCl_3 + 2\ CO + 5/2\ Cl_2$

The $PuCl_3$ is obtained as a sublimate and the reaction is carried out in a quartz system. There is visual evidence of slight attack on the quartz where the $PuCl_3$ first condenses on it. At 600° to 700°C. in a Cl_2, CCl_4 mixture, the conversion may be carried out so that much of the material does not sublime.

(g) $PuO_2 + 3/2\ SCl_2$ (ca. 800°C.) $= PuCl_3 + SO_2 + 1/2\ S_2$

The $PuCl_3$ is obtained as a sublimate. The sulfur content of an 8 mg. sample of $PuCl_3$ made by this method was found to be about 2800 ppm. The sublimed product obtained by methods (f) and (g) is green in color. "Gently ignited PuO_2" or $PuO_2 \cdot xH_2O$ is most suitable for these reactions.

(h) Liquid phase halogenation of $PuO_2 \cdot xH_2O$ at 280°C. using PCl_5, CCl_4 plus several per cent Cl_2, or S_2Cl_2 plus several per cent Cl_2 produces $PuCl_3$.

(i) $PuCl_3 \cdot 6H_2O$, obtained from aqueous solution, may be dehydrated in vacuo at room temperature to $PuCl_3 \cdot H_2O$. The monohydrate may be slowly converted to $PuCl_3$ in vacuo at 70°C. The product was identified only by the X-ray method and its purity with respect to PuOCl or PuO_2 is not known.

Plutonium trichloride is converted to PuO_2 upon heating in air to about 400°C. but is stable with respect to air oxidation at room temperature. It dissolves rapidly in water to give a clear solution with the purple color characteristic of Pu(III).

On the basis of the non-reducibility of $PuCl_3$ by Ce, the heat of formation of $PuCl_3$ was estimated as greater than that of $CeCl_3$ and as

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probably 265 to 270 kilocalories. The melting point and vapor pressures of $PuCl_3$ are reported in Table III-12 at the end of this section.

2. Hydrates of $PuCl_3$. The established facts about the hydration of $PuCl_3$ in non-equilibrium systems are contained in Table III-10.

Table III-10. Interconversion of $PuCl_3$ Hydrates in Non-Equilibrium Systems

Initial Compound	Temp. °C.	H_2O Pressure (mm.)	Final Compound
$PuCl_3$	25	1	$PuCl_3 \cdot H_2O$
$PuCl_3 \cdot H_2O$	70	10^{-5}	$PuCl_3$
$PuCl_3 \cdot H_2O$	25	4	$PuCl_3 \cdot 6H_2O$
$PuCl_3 \cdot 3H_2O$	25	10^{-5}	$PuCl_3 \cdot H_2O$
$PuCl_3 \cdot 6H_2O$	25	1	$PuCl_3 \cdot 3H_2O$

$PuCl_3 \cdot 6H_2O$ is deliquescent and melts at 94° to 96°C. X-ray examination shows that $PuCl_3 \cdot 6H_2O$ is isomorphous with $NdCl_3 \cdot 6H_2O$.

3. PuOCl. When heated to 400° to 600°C. in a small sealed tube, $PuCl_3 \cdot 6H_2O$ is converted to PuOCl together with some $PuCl_3$ or PuO_2. This compound is a green or blue-green solid which is insoluble in water, but soluble in dilute acids.

The synthesis of $PuCl_3$ from PuO_2 by means of an H_2, HCl vapor mixture may be considered to involve the two consecutive reactions:

$$PuO_2 + 1/2\ H_2 + HCl = PuOCl + H_2O$$

$$PuOCl + 2\ HCl = PuCl_3 + H_2O$$

The following facts have been established about the equilibria in these two equations:

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(a) A sample of $PuO_2 \cdot xH_2O$, treated at 675°C. with a vapor of composition 570 mm. HCl, 190 mm. H_2 and 4 mm. H_2O, was converted to $PuCl_3$ in four hours.

(b) Samples of $PuCl_3 \cdot 6H_2O$ or PuOCl treated at 650°C. with vapor of the composition 640 mm. HCl, 120 mm. H_2, and about 0.2 mm. H_2O for four hours were found to be PuOCl. Equilibrium was probably not obtained in these experiments, due perhaps to a form of PuOCl that reacts only very slowly to give $PuCl_3$.

(c) With a vapor of the composition 85 mm. HCl, 680 mm. H_2 and 7.3 mm. H_2O, $PuCl_3 \cdot 6H_2O$ was converted to PuOCl.

4. $PuCl_4$. As yet no anhydrous $PuCl_4$ of proven identity has been prepared. If $PuBr_3$ is treated with liquid Cl_2 at 140°C. and 70 atmospheres pressure, only $PuCl_3$ is formed. If $PuO_2 \cdot xH_2O$ is treated with a mixture of liquid CCl_4 and Cl_2 at 280°C. and cooled to room temperature, where the volatile components are removed, only $PuCl_3$ is observed. Attempted "wet" preparations of $PuCl_4$, i.e., preparations in which a $PuCl_4$ solution is evaporated in a stream of HCl, have given rise to phases with unidentified crystal structures. Some of these preparations have a high Cl to Pu ratio (six or greater) and often contain $PuCl_3$. It is probable that if $PuCl_4$ exists at all, it is very unstable relative to decomposition into $PuCl_3$ and Cl_2.

There is some evidence that $PuCl_4$ solutions evaporated to dryness in air at 50°C. give a material which is primarily $PuOCl_2$. This latter material is not reduced readily with H_2, but an H_2, HCl mixture converts it to $PuCl_3$.

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Bromide Compounds.--

1. $PuBr_3$. Tribromide has been prepared according to the following reactions:

(a) $Pu + 3/2\ Br_2$ (ca. 400°C.) = $PuBr_3$

With a chlorine-free bromine the normal orthorhombic form of $PuBr_3$ is obtained; bromine that was not especially purified gave rise to a substance with the hexagonal crystal structure typical of $PuCl_3$ and $LaBr_3$ and a composition estimated from the X-ray data to be $Pu(Br_{0.8}Cl_{0.2})_3$.

(b) $PuO_2 + 4\ HBr$ (ca. 600-800°C.) = $PuBr_3 + 2\ H_2O + 1/2\ Br_2$

In this preparation it is preferable to use a finely divided PuO_2, such as that obtained by igniting $Pu(NO_3)_4$ to 300°C. or less, or the $PuO_2 \cdot xH_2O$ obtained by oven-drying plutonium(IV) hydroxide at 70°C. Plutonium tribromide made by this reaction gives a better analysis and contains less water insoluble material if it is carried out in a platinum boat rather than in contact with quartz.

(c) $Pu(C_2O_4)_3 \cdot 9H_2O + HBr$ (ca. 600°C.) = $PuBr_3 +$ {Unidentified volatile products}

This method appears to be the preferable one for production of large quantities of $PuBr_3$.

(d) Solutions of $PuBr_4$ are slowly reduced to $PuBr_3$ solutions at 70°C. by HBr. If such solutions are evaporated to dryness in a stream of HBr at about 10 mm. pressure, the $PuBr_3 \cdot xH_2O$ formed can be dehydrated in a stream of HBr by gradually heating to 225°C. or higher to yield $PuBr_3$.

(e) $PuO_2 + 1/2\ S_2 + 3/2\ Br_2$ (800°C.) = $PuBr_3 + SO_2$

The $PuBr_3$ is obtained as a sublimate. The bromine and sulfur pressures

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were about 100 mm. and 50 mm., respectively.

(f) $PuBr_3$ may also be prepared by treating $PuCl_3$ with HBr vapor at 750°C.

Plutonium tribromide takes up water vapor from the atmosphere to form $PuBr_3 \cdot 6H_2O$. The hexahydrate is deliquescent, and $PuBr_3$ or its hydrate dissolves in H_2O to give a clear solution with the characteristic Pu(III) color. It does not react with Br_2 to form $PuBr_4$ at any temperature from room temperature to 400°C. It is not reduced by H_2 at 800°C., and at 200°C., O_2 converts it to PuO_2. The salt as obtained by the "high temperature methods" (b, c and e above) is green, but the material obtained at lower temperatures by bromination of metal is blue or blue-green in color. Plutonium tribromide has been sublimed in S_2, Br_2 vapor mixture (150 mm. pressure) at 800°C. and in an atmosphere of HBr at 1000°C. or less. Some sublimation is observed in the preparations of $PuBr_3$ using HBr at 750° to 800°C. Melting point and vapor pressure data are given in Table III-12 of this section.

2. PuOBr. Table III-11 contains a summary of the studies of the hydrobromination of $PuO_2 \cdot xH_2O$ that have been carried out with a controlled vapor mixture of H_2, HBr and H_2O in a study of equilibria in the reactions:

(a) $PuO_2 + 1/2\ H_2 + HBr = PuOBr + H_2O$

(b) $PuOBr + 2\ HBr = PuBr_3 + H_2O$

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Table III-11.

Hydrobromination of $PuO_2 \cdot xH_2O$ by Mixtures of Hydrogen, Hydrogen Bromide and Water Vapor

Exp. No.	Starting Material	$P(H_2O)$ (mm.)	$P(HBr)$ (mm.)	$P(H_2)$	Product	Remarks
1	$PuO_2 \cdot xH_2O$	22	5	230	PuO_2	800°C., 4 hrs.
2	"	1.9	27	230	PuOBr	"
3	"	0.1*	760	-	$PuBr_3$	750°C., 6 hrs.
4	"	0.1*	400	-	PuOBr	" 7 hrs.
5	"	0.38*	117	-	"	" "

* These water pressures were obtained by bubbling HBr at the stated pressure through a saturated aqueous solution at 25°C. The water pressures were estimated by extrapolation from a curve of H_2O pressure against HBr pressure for aqueous solutions with a lower HBr pressure (International Critical Tables, Vol. 3, p. 306).

If it is assumed that equilibrium was attained in these experiments, approximate equilibrium constants for reactions may be calculated. From experiments 1 and 2, the equilibrium constant for reaction (a) at 800°C. is bracketed between 9.1 and 0.13 (pressures expressed in atmospheres). From experiments 3 and 4, the equilibrium constant for reaction (b) is bracketed between 1.3×10^{-4} and 5×10^{-4}. It is important to note that it is not necessary to add H_2 to the HBr for the conversion of PuO_2 to $PuBr_3$, while H_2 is necessary with HCl for the production of $PuCl_3$. This is because HBr is a stronger reducing agent than HCl.

PuOBr may be obtained by use of the appropriate vapor mixture as indicated in Table III-11. An impure preparation has been obtained by the reaction:

$$PuO_2 + PuBr_3 \ (800°C.) = 2\ PuOBr + 1/2\ Br_2$$

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An atmosphere of argon was used to decrease the distillation of $PuBr_3$.

PuOBr is a green compound, insoluble in H_2O and soluble in dilute acids.

Iodide Compounds.--

1. PuI_3 and PuOI. The green triiodide has been prepared by the action of HI vapor on Pu metal at 425°C. and identified by X-ray analysis and by chemical analysis.

Treatment of PuO_2 with HI vapor at 750°C. gave rise only to the green PuOI. An attempted "wet" preparation in which a PuI_3, NH_4I solution was evaporated to dryness in a stream of HI (60 mm.) at 60°C. and then slowly heated to 350°C. in the HI stream to sublime away the NH_4I, gave rise only to PuOI. Attempts to make PuI_3 by treatment of a PuO_2 and lampblack mixture with a stream of HI at 1000° to 1400°C. gave no volatile reaction product; attempts to make PuI_3 by treatment of PuO_2 with AlI_3 vapor or liquid were not successful.

Vapor Pressures and Melting Points of the Oxides and Halides

Technique of Measurements.— Vapor pressure measurements were carried out by an effusion method in an evacuated Pyrex envelope. A tantalum oven having a small orifice of about 0.15 mm. diameter contained the sample and was induction heated. The effusing molecular beam was collimated and deposited on a liquid air cooled target plate

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above the collimator.

Methods were provided for exposing the target to the molecular beam for a given time at a known temperature, and then for replacing the exposed target with a new one without breaking the vacuum or cooling the furnace. Approximately fifty targets were loaded into the apparatus at a time. Any desired number of exposed targets were removed from the apparatus by the simple process of sealing off a constriction in a Pyrex tube. Weighing the target deposit was accomplished by counting its alpha activity.

Vapor Pressure and Related Data.-- The available preliminary vapor pressure data for the oxides and halides of plutonium which have been studied are collected in Table III-12. Wherever it seemed justified by the data, the method of least squares was used to obtain values of the constants A and B in the usual equation for the vapor pressure, $\mathrm{Log}_{10} p = A - B/T$.

In the case of the halides, two intersecting straight lines were obtained by plotting log P vs. 1/T corresponding to vapor pressures of the solid and the liquid states. From this analysis of the data the heats of vaporization from the liquid, ΔH_{liq}, the heat of sublimation from the solid, ΔH_{sol}, and the heats of fusion were calculated. The melting points were taken as the temperatures of intersection of the straight lines on the log p vs. 1/T plot. The data on each compound are discussed separately.

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Table III-12. Vapor Pressures of Plutonium Oxides and Halides

Temp. °K.	Pressure in mm. of Hg x 10^6				
	PuO_2-"Pu_2O_3"*		PuF_3	$PuCl_3$	$PuBr_3$
800					0.97
850					13.0
900				7.98	130.6
950				67.5	853.0
1000				460.3	3805.
1050				2017.	14690.
1100				6967.	50170.
1150			0.88	21580.	
1200			5.34	60960.	
1250			28.0		
1300			129.0		
1350			532.0		
1400			1982.		
1450			6239.		
1500			17450.		
1550			45690.		
1600	0.144	0.35	112600.		
1650	0.55	1.09	262100.		
1700	1.95	3.47			
1750	6.41	10.3			
1800	19.7	28.8			
1850	57.5	76.2			
1900	158.	191.			
1950	410.	458.			
2000	1021.	1048.			
2050	2425.	2309.			
K cal/mol					
ΔH_{sol}	141.1	128.6	98.73±0.42	72.52	70.11±0.25
ΔH_{liq}			88.89±0.40	56.88	56.69±0.14
ΔH_{fusion}			9.84±0.56	15.64	13.43±0.29
M.P. °C.			1141 ± 7	742.	654 ± 4
	Vapor Pressure Equation: $Log_{10}\ p = A - B/T$				
A_{sol}	12.42	11.08	12.71	12.51	13.13
$B_{sol} \times 10^{-4}$	3.083	2.812	2.158	1.585	1.532
A_{liq}			11.20	9.14	9.97
$B_{liq} \times 10^{-4}$			1.943	1.243	1.239

* See "Plutonium Oxides" in text.

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1. Plutonium Oxides. The values given for PuO_2 and "Pu_2O_3" were obtained for a sample which was originally PuO_2. Before this sample had been heated to a high temperature, i.e., in the ascending temperature measurements, the vapor pressures given in Table III-12, under PuO_2, followed one straight line on a log p vs. 1/T plot, but after reaching the higher temperatures the data followed a different straight line of lower slope but slightly higher vapor pressure when the curve was repeated. In view of the known fact that PuO_2 decomposes on tantalum at high temperatures in a high vacuum yielding "Pu_2O_3", this data is listed under "Pu_2O_3" although it is probably far from being pure "Pu_2O_3".

2. Plutonium Trifluoride. The data on the fluoride scattered very little from two intersecting straight lines on a log p vs. 1/T plot. The indicated melting point is given in the Table.

3. Plutonium Trichloride. The initial data showed evidences of a more volatile impurity which gradually distilled out. The final data settled down to two intersecting lines with a melting point at 742°C. This is considerably lower than the melting point of 760°C. obtained for sublimed chloride by direct observation. Apparently the chloride sample was quite impure. To obtain better results, it will probably be necessary to sublime a sample into the crucible, all operations being carried out in a high vacuum.

4. Plutonium Tribromide. The bromide also showed some indications of a more volatile constituent being present at the beginning of the heating. This was by far not as pronounced as in the chloride experiments. The indicated melting point of 654°C. is, however, lower than the melting

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point of 681°C. as determined by direct observation on sublimed material.

MISCELLANEOUS COMPOUNDS OF PLUTONIUM

This section contains the available information as to the preparation and properties of some of the compounds of plutonium other than the halides and oxyhalides. The compounds prepared and characterized to date are: the Pu hydrides and deuterides, PuN, the Pu carbides, $PuSi_2$, Pu_2S_3 (or Pu_3S_4), Pu_2O_2S, an impure PuS, and Pu(IV) acetylacetonate.

Plutonium Hydride and Deuteride

Plutonium metal at room temperature will take up hydrogen or deuterium with the evolution of heat. The lump of metal disintegrates during reaction and some particles of hydride are thrown off the metal piece with sufficient velocity to scatter them a distance of several centimeters. The reaction with hydrogen at room temperature may show an induction period of some minutes or may be almost instantaneous. The powdered hydride is a shiny black and more or less metallic in appearance. It presumably will react vigorously with air and H_2O and in general may be expected to undergo reactions with NH_3, CH_4, HCl, HBr, etc. similar to those observed with UH_3.

Isotherms for the Hydrogen-Plutonium System.-- A careful study has been made of the pressure of hydrogen as a function of composition of the hydride and of the temperature. At 25°C. and a hydrogen pressure of 200 mm., the formula is $PuH_{2.97}$. The composition changes markedly with pressure; at 25 mm. the composition is $PuH_{2.93}$ and at 24 mm. $PuH_{2.89}$. However, below the composition $PuH_{2.0}$ the pressure is independent of composition. The data are recorded in Table III-13.

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Table III-13. Pressure-Temperature-Composition Data for Plutonium Hydride

25°C.		100°C.		160°C.		200°C.		300°		400°		500°	
H/Pu	P mm.	H/Pu	P	H/Pu	P	H/Pu	P	H/Pu	P	H/Pu	P	H/Pu	P
2.97	200	2.90	153	2.87	364	2.79	354	2.60	405	2.45	245	2.29	160
2.93	22	2.88	88.8	2.82	87	2.75	231	2.55	148	2.31	25.4	2.15	19
2.92	9.5	2.83	8.0	2.77	61.5	2.70	126	2.47	39	2.15	2.2	2.04	2.5
2.91	8.8	2.78	4.4	2.71	15	2.64	41.7	2.31	0.8	2.04	1.4		
2.89	2.5	2.71	1.0	2.64	10	2.56	6.0						
2.83	0.4	2.65	1.0	2.56	1.4	2.48	1.4						
							*	1.97	0.0003	1.97	0.008	1.97	0.364
										1.27	0.008	1.27	0.362
										0.66	0.008	0.66	0.365
										0.29	0.008	0.29	0.364
												0.006	0.018

* From this point on, pressures were measured by means of a McLeod gauge.

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Isotherms for the Pu, H_2 systems are plotted in Figures III-22 and III-23. The constancy of pressure with changing H/Pu atom ratio below 2 shown in the 400° and 500°C. isotherms of Figure III-23 indicate that when the atomic ratio is below 2 the reaction is

$$Pu + H_2 = PuH_2;$$

the Pu and PuH_2 being separate phases. In the region from H/Pu = 2 to H/Pu = 3 the reaction may be considered as

$$PuH_2 + 1/2\ H_2 = PuH_3;$$

the PuH_2 and PuH_3 being in solid solution in one another. The shapes of the isotherms in Figures III-23 and III-22 indicate that at higher pressures of hydrogen, ratios greater than 3 may be obtained, although rather large pressures would be required to increase the ratio significantly. At room temperature, the ratio reaches 3 at a hydrogen pressure of about 350 mm. as estimated by extrapolation of the existing data.

Equilibrium Hydrogen Pressures as Function of Temperature.--
Pressure-temperature curves showing the relation between log p and 1/T are given in Figure III-24 for three compositions: H/Pu = 1.97, 2.60 and 2.87. The values used in drawing these curves were taken from the isotherms given in Figures III-22 and III-23. The equations for the best straight lines through the points are:

For H/Pu = 1.97 $\log_{10}p(\text{mm.}) = -7.13 \times 10^3\ (1/T) + 8.77$

H/Pu = 2.60 $\log_{10}p(\text{mm.}) = -4.17 \times 10^3\ (1/T) + 9.9$

H/Pu = 2.87 $\log_{10}p(\text{mm.}) = -2.7 \times 10^3\ (1/T) + 8.8$

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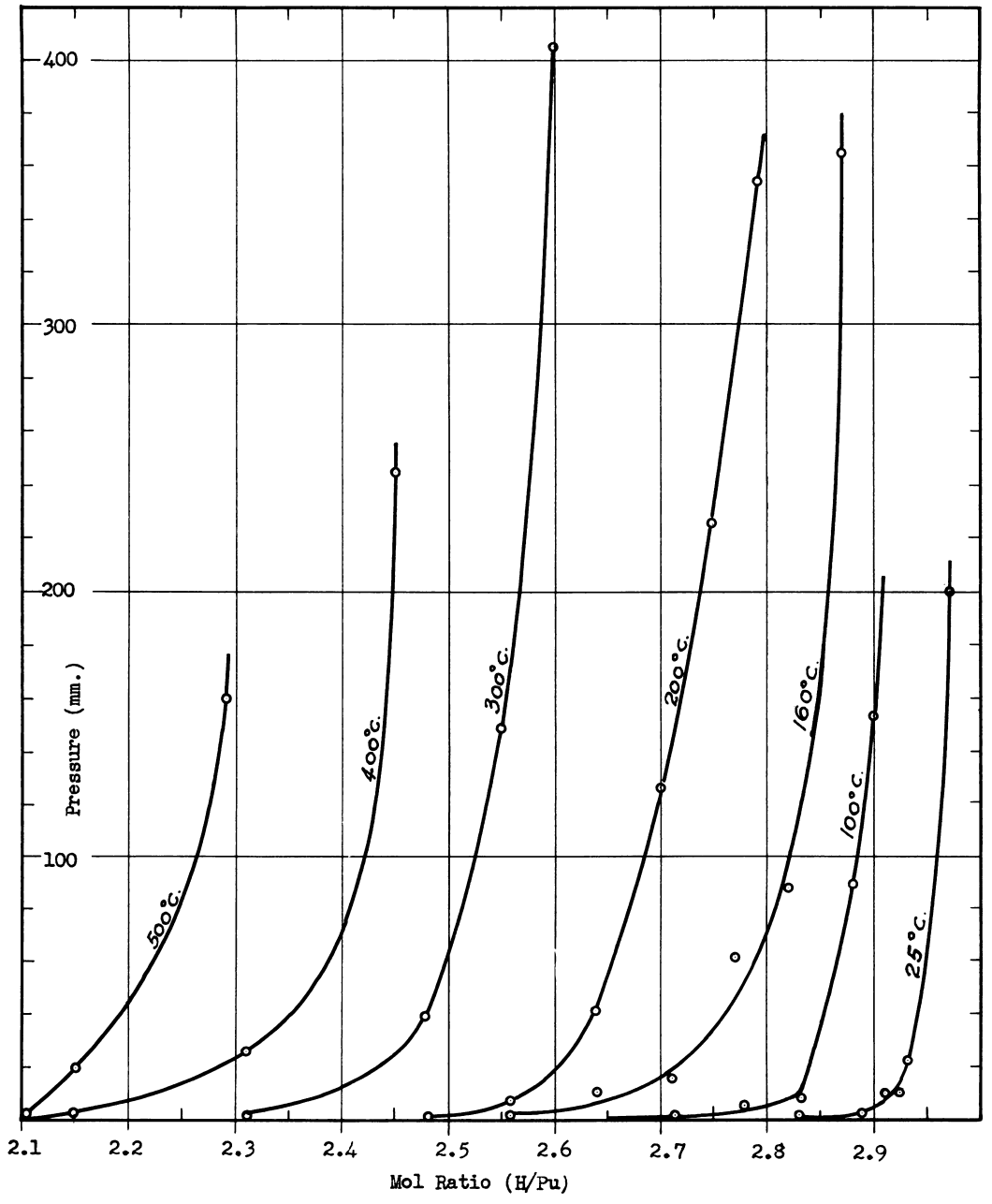

Fig. III-22. Isotherms of the H_2-Pu System

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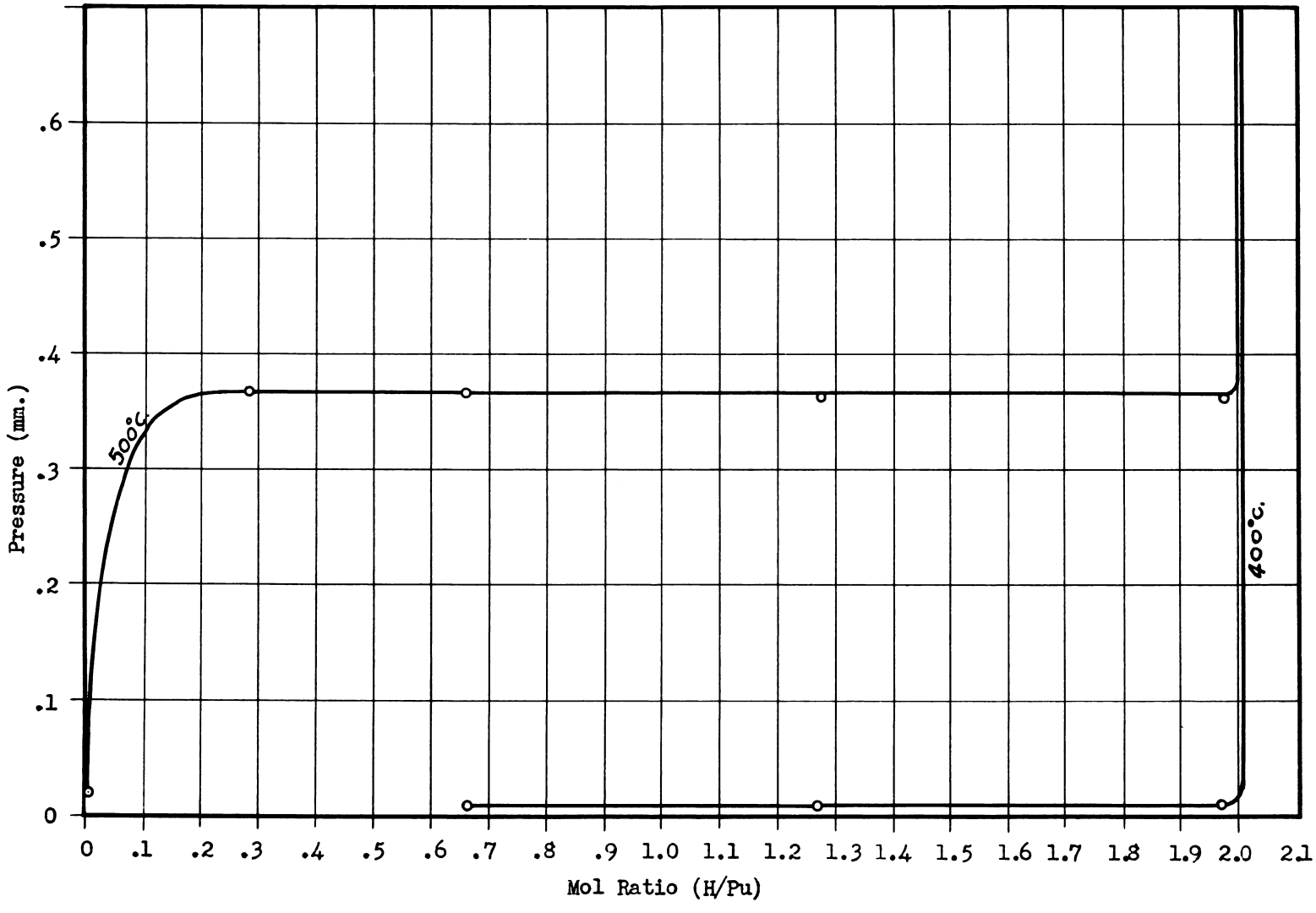

Fig. III-23. Isotherms of the H_2-Pu System

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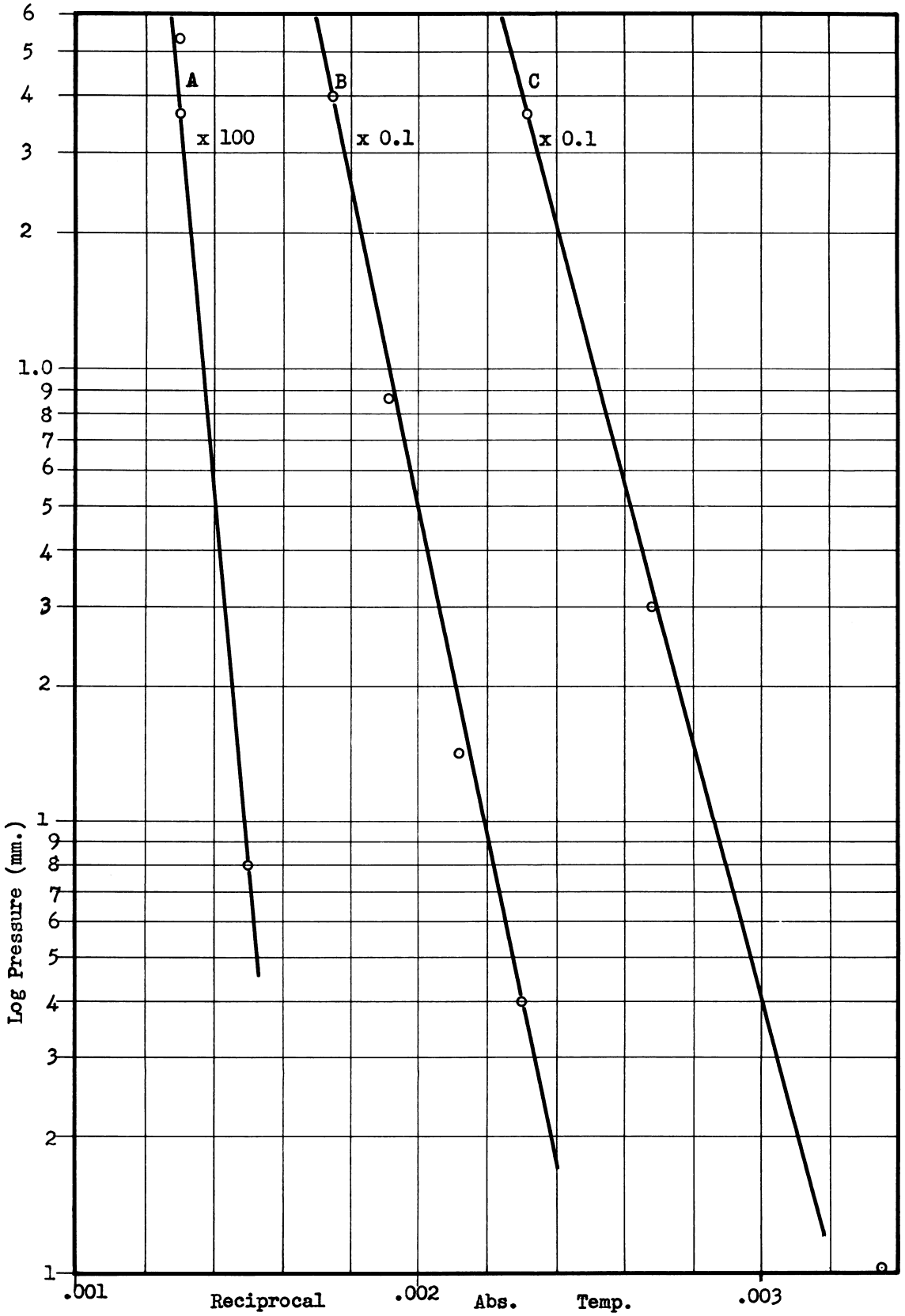

A - H/Pu = 1.97 B - H/Pu = 2.60 C - H/Pu = 2.87

Fig. III-24. Log P vs 1/T for H_2-Pu System

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From the slope of the first line corresponding to the reaction

$$Pu + H_2 = PuH_2$$

one may calculate a value of $\Delta H = -32,500$ cal. per mol for the reaction. From the slopes of the other two lines, one may calculate that 9550 and 6180 calories are absorbed when 1/2 mol of H_2 gas is removed from a very large amount of $PuH_{2.60}$ and $PuH_{2.87}$, respectively. Another way of stating this is that for the reaction

$$PuH_2 + 1/2\ H_2 = PuH_3$$

$\Delta H = -9550$ and -6180 cal. per mol, when the PuH_2 and PuH_3 are in solid solutions at the composition $PuH_{2.60}$ and $PuH_{2.87}$, respectively.

Plutonium Deuterides.-- The substitution of deuterium (99 per cent) in place of hydrogen in the above experiments yields similar results. At room temperature under 9 mm. D_2 pressure, the atomic ratio D/Pu was found to be 2.8. At a composition corresponding to a D/Pu ratio of 1.95, the pressure at 400°C. was 0.01 mm. and at 500°C. it was 0.533 mm. These pressures are higher than the pressures of hydrogen over the hydride at the same temperature. The curve for log p as a function of (1/T) is parallel to that for the hydride; accordingly the heat of reaction is approximately the same for the deuteride as for the hydride. The 500°C. isotherm for the deuteride is parallel to that for the hydride, the pressures at corresponding compositions being 1.45 and 1.50 times greater for D_2 than for H_2.

Many attempts have been made to prepare a sample of plutonium hydride suitable for X-ray analysis, but all of these preparations have shown only the X-ray pattern of PuO_2. This may have been due to a

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PuO_2 coating on the hydride particles or it may imply that the hydride formed was always amorphous. Presumably, however, the phase PuH_2 is crystalline with a definite crystal structure.

Plutonium Nitride

The nitride, PuN, has been made by the two orthodox reactions listed below and identified by means of its X-ray diffraction pattern.

(a) $Pu + 1/2\ N_2 + 3/2\ H_2(\text{from } NH_3)\ (1000^\circ C.) = PuN + 3/2\ H_2$

(b) $PuCl_3 + 1/2\ N_2 + 3/2\ H_2(\text{from } NH_3)\ (800\text{-}900^\circ C.) = PuN + 3\ HCl$

It has also appeared as a minor phase among the products obtained by an attempted atomic hydrogen reduction of PuF_3.

The reaction between Pu metal (about 5 mg.) and anhydrous NH_3 gas (250 mm.) was carried out on an electrically heated platinum filament at 1000°C. The formation of a brown coating of PuN on the metal was observed under a microscope. The metal, however, did not completely react. The reaction between nitrogen and massive metal, even in the molten state, is apparently sluggish, since some of the metal melted and wet the platinum filament without reacting to yield PuN.

When plutonium hydride (formed at room temperature and an H_2 pressure of 20 cm. of Hg) is exposed to NH_3 at 25 cm. pressure and heated to 600°C., followed by slow cooling to room temperature, only PuN is formed. Under similar conditions, UH_3 forms "higher" nitrides such as $UN_{1.75}$.

The preparation of PuN from $PuCl_3$ was carried out by passing a slow stream of anhydrous NH_3 over $PuCl_3$ in a platinum boat in a quartz tube.

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The temperature of the sample was slowly raised from 800° to 900°C. over a period of an hour and maintained at 900°C. for 15 minutes. X-ray analysis showed that the product contained about 50 per cent PuO_2, 35 per cent PuN, and 10 per cent PuOCl. By analogy with the reaction

$$CeCl_3 + 1/2\ N_2 + 3/2\ H_2 = CeN + 3\ HCl$$

for which some thermodynamic data are available, it may be assumed that the pressure of HCl in equilibrium with $PuCl_3$ and the N_2, H_2 mixture is probably only a fraction of a centimeter at 800° to 900°C., and the HCl must be continuously swept out in the gas stream to prevent reversal of the reaction. The fact that the reaction proceeds at all indicates that the heat of formation of PuN is certainly greater than 50 kcal. per mol and probably greater than 75 kcal. per mol (that for CeN is 78 kcal. per mol).

Plutonium Carbide

Plutonium monocarbide, PuC, was identified by X-ray analysis as the principal product of a vapor phase reduction of PuF_3 with Ca vapor at 1200°C. in a graphite crucible, on the 5 mg. scale. There was some indication of another phase which may have been Pu_2C_3.

When PuO_2 (50 mg.) was ground with excess graphite and the mixture heated in a tungsten crucible in vacuo to 1200° to 1500°C., CO was evolved in accordance with the equation

$$(2+X)C + PuO_2 = 2\ CO + PuC_X$$

The chemical composition of the carbide obtained has not been ascertained. When this carbide is heated to 1900° to 2200°C., Pu metal

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distills out of the carbide. Plutonium metal is distilled out in the temperature range 1200° to 1500°C. if only the stoichiometric quantity of carbon required by the following reaction is present:

$$2\ C + PuO_2 = Pu(vapor) + 2\ CO$$

Plutonium dioxide when heated on a platinum filament to 1500°C. in a slow stream of CH_4 (250 mm.) does not form carbide, although considerable carbon black deposits on the filament.

Plutonium Silicide

Plutonium disilicide, $PuSi_2$, is a lustrous, silvery metallic appearing compound, which readily flakes into platelets. Its identification is based on X-ray analysis. This compound has been obtained by the reduction of PuF_3 with $CaSi_2$. It was found that both Ca and Si are volatilized from $CaSi_2$ at 1550°C., so vapor phase reductions with double crucible systems are feasible with this reductant.

In non-vapor phase reduction, when the reactants are mixed according to the equation

$$10\ PuF_3 + 3\ CaSi_2 = 10\ Pu + 3\ CaF_2 + 6\ SiF_4$$

no reaction occurs at 1300°C., but at 1550°C. reaction occurs to yield $PuSi_2$. No Pu metal was obtained. It seems probable that the synthesis proceeds according to the equation

$$PuF_3 + 1.1\ CaSi_2 = PuSi_2 + 1.1\ CaF_2 + 0.2\ SiF_4$$

Air ignition of $PuSi_2$ at 700°C. converts it to a substance which shows only the X-ray diffraction pattern of PuO_2. Attempts to reduce PuO_2 with $CaSi_2$ in the presence of a Na_2CO_3 flux gave rise only to Na

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vapor and no reaction with the PuO_2 to yield either metal or silicide.

Plutonium Sulfides and Oxysulfide

The phase "Pu_2S_3-Pu_3S_4" was obtained by treatment of $PuO_2 \cdot xH_2O$ in a graphite crucible with H_2S at about 1400°C. for two hours. The identification is based on X-ray analysis. The substance was a black powder.

By treatment of $PuO_2 \cdot xH_2O$ in a similar fashion with H_2S at about 1300°C. for one-half hour, the phase Pu_2O_2S (identified by X-ray analysis) was obtained.

These compounds are isomorphous with the cerium compounds, Ce_2S_3-Ce_3S_4, and Ce_2O_2S. CeO_2 treated with H_2S at 1400°C. in a graphite system gives rise to Ce_2S_3. Ce_2S_3 heated in vacuum to 2000°C. is slowly "vacuum reduced" to the composition Ce_3S_4 with the same crystal structure as Ce_2S_3 but a slightly smaller lattice constant. In view of the analogy in the methods of preparation, the plutonium compound is probably Pu_2S_3.

A vapor phase reduction of PuF_3 with calcium in a BaS crucible at 1350°C. yielded a metallic appearing golden bronze colored material. A combination of X-ray and chemical evidence indicated that this was probably an impure PuS preparation containing some BaS in solid solution. Air ignition of the sample at 700°C. caused no detectable change in weight but the appearance of the material changed to that of a black powder. The powder showed only the X-ray pattern of PuO_2.

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Plutonium(IV) Acetylacetonate

The formula of Pu(IV) acetylacetonate has been reasonably well established as $Pu(C_5H_7O_2)_4$, corresponding to a Pu(IV) coordination number of eight. The compound is precipitated as reddish-brown crystals by the addition of an NH_4OH solution of acetylacetone to a H_2SO_4 solution of Pu(IV) followed by the addition of NH_4OH to bring the pH in the range 9 to 10. The precipitated compound may be purified by re-crystallization from C_6H_6 or by sublimation at about 170°C. in vacuo.

A melting point of a sublimed sample of 170° to 173°C. has been observed with some evidence of slight decomposition. At 140°C., an approximate vapor pressure of 10^{-4} mm. was found as compared with a similar pressure reported for $Th(C_5H_7O_2)_4$ at about 100°C. Sublimation of $Pu(C_5H_7O_2)_4$ at about 170°C. in vacuo has been very useful in the preparation of thin Pu coated foils for purposes of physical measurements.

The compound is soluble in $CHCl_3$ and C_6H_6 and may be directly extracted into $CHCl_3$ from aqueous solutions of suitable pH. Using equal volumes of $CHCl_3$ and aqueous phase, the following percentages of Pu may be extracted into the $CHCl_3$ at the pH values given: 21 per cent at pH = 2; 79 per cent at pH = 3; and 94 per cent at pH = 4.

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ESTIMATE OF ELECTROPOSITIVE CHARACTER OF PLUTONIUM

Tracer Distribution of Plutonium Between Metal and Salt Phases

The general purpose of the experiments discussed below was to fix the oxidizing-reducing power of the plutonium : plutonium halide couple relative to certain other metal : metal halide couples at elevated temperatures under conditions comparable with those obtaining in bomb reductions and fused salt electrolysis. Specifically, there were two main aspects of the work. First was the direct comparison of corresponding plutonium and uranium couples. This comparison was designed to test an assumption that seemed most useful in preparing plans in advance of actual metal production, namely, that the two elements are sufficiently similar to justify the expectation that metallurgical practices developed for uranium might be taken over, in broad outline, for plutonium. The second aspect was the attempt to bracket both plutonium and uranium by a graded series of couples which would fix their position in a "replacement series" in the halide systems. Such information is necessary for appropriate choice or control of reductants, fluxes, fused salt baths, and refractories to be employed in working processes.

Experimental Procedures.-- The experimental procedure in all cases was to equilibrate a system consisting of a metal and one of its molten anhydrous halides with plutonium tracer at some constant high temperature in an atmosphere of helium or argon in a container of appropriate material sealed in a silica tube. At the end of the equilibration period the system was cooled, the metal and salt phase separated and the

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distribution of the plutonium tracer between them determined by appropriate counting techniques. At temperatures below the melting point of the metal under comparison, this metal itself was generally employed as container for the salt. For liquid metals, a container of some other material, as inert as possible under the conditions of use, was needed. The tracer was usually introduced incorporated in the anhydrous salt; sometimes it was originally distributed through the metal itself; and sometimes it was deposited from tracer solution by evaporation on the surface of the container, or upon the surface of inert metallic strips introduced into the container. It was considered, and seemed to be confirmed experimentally, that reaction would be rapid if contact was good and that when both metal and salt were liquid, gentle stirring for periods of the order of an hour would give a close approach to equilibrium. For solid metals it was assumed that the surface of the metal would at all times be in substantial equilibrium with the body of the stirred liquid. The problem of determining the surface condition was met, when possible, by dissolving (or etching) successive layers, or by machining off successive layers for separate counting and extrapolating to the surface condition when necessary.

Expression of Direct Results.-- The experimental result was always expressed in the form of a ratio k_M characteristic of the system, where k_M = (tracer counts per mol salt)/(tracer counts per mol metal). This ratio will be referred to as the "equilibrium ratio". Its relation to the equilibrium constant of the various reactions is discussed below.

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It should be noted now, however, that a value of unity for k_M (or related equilibrium constants) indicates equal strength of the couples concerned. Values of k_M larger than unity mean that the plutonium (or, in general, the tracer) couple is the stronger reducing agent, or the more electropositive.

In calculating k_M, the number of moles of salt was always taken as the number of gram atoms of the constituent metal in the salt phase, and for the liquid metals the mol was assumed identical with the gram atom. Experimentally, there was always significant "solubility" of the test metal in its salts. Although the dihalide and trihalides were always used as the starting substances, at equilibrium the single phase liquid would be richer in metal. On freezing, the "dissolved" metal always separated, generally in finely dispersed form. When feasible, this finely dispersed metal was counted as part of the salt phase in calculating k_M.

Collected Results of Tracer Experiments.-- The results of all experiments from which a numerical result was obtained are recorded in Table III-14. The metals compared, directly or indirectly, with plutonium are uranium, thorium, cerium, lead, manganese, magnesium, calcium, strontium and barium.

Experimentally, the values of the equilibrium ratio in Table III-14 are not all equally reliable. For example, the first uranium experiments (1) were the only ones done without stirring. The third uranium result (3) was obtained by extrapolation from a particularly reliable series of determinations of the final depth distribution of tracer originally

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Table III-14.

Equilibrium Ratios (k_M) in Reactions of Plutonium, Uranium and Thorium Tracers with Metals and their Molten Halides

Line No.	System*	Container	No.Expts.	Time (hrs.)	Temp.°C.	k_M
(1)	U : UBr_x : Pu	Mullite Porcelain	3	2	900	16
(2)	"	" "	3	1-2	1140	28
(3)	"	U	1	2	1000	40
(4)	U : UBr_x : Th	U	2	1-4	1000	1.4
(5)	Ce : $CeBr_x$: Pu	Mo	4	3	790-800	0.3
(6)	Pb : $PbCl_x$: Pu	SiO_2	4	2-5	550-700	310
(7)	Mn : $MnCl_x$: Pu	Pt	5	¼-2	730	8.7
(8)	"	Al_2O_3	1	3	720	8.3
(9)	Mg : $MgBr_xI_y$: Pu	Fe	1	3	675	63
(10)	Mg : MgI_x : Pu	Fe	7	3	700	92
(11)	Mg : $MgCl_x$: Pu	Fe	1	2	760	17
(12)	Mg : $MgCl_x$: U	Fe	1	2	760	7.5
(13)	Mg : $Mg(Br,I)_2$: Pu	Mg	1	4	632	5.6
(14)	Mg : $Mg(Cl,I)_2$: Pu	Mg	3	3-5	622	0.92

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Table III-14, Continued

Line No.	System*	Container	No.Expts.	Time (hrs.)	Temp.°C.	k_M
(15)	Mg : $Mg(Cl,I)_2$: <u>U</u>	Mg	2	5	622	0.72
(16)	Ca : $CaCl_x$: <u>Pu</u>	Ca	3	2	820	0.17
(17)	"	Fe	1	8	900	0.85
(18)	"	Ca	1	6	820-840	2.2
(19)	"	Ca	1	6	800	1.7
(20)	"	Ca	1	6	800	0.14
(21)	"	Ca	1	4	800	0.2
(22)	Sr : $SrBr_x$: <u>Pu</u>	Fe	1	5	811	0.24
(23)	"	Sr	1	3	708	0.25
(24)	"	U	1	3	820	0.13
(25)	Ba : $BaBr_x$: <u>Pu</u>	Fe	1	3	887	1.3
(26)	"	FeCr	1	3	915	6
(27)	"	Fe	1	5	905	1.1
(28)	"	U	2	3-5	903	1.1
(29)	"	U	2	5	910	0.3

* Trace element is underlined.

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uniform throughout the uranium capsule container. The lead : lead chloride constant is so large that it cannot be accurately determined by this technique. The average value of 310 given in the Table should be interpreted merely as a large number, that is, the plutonium couple is a very much stronger reductant than the lead couple. The manganese system gave self-consistent results, yet is affected by numerous uncertainties. The metal employed was in granular porous cathode sheets, and the granules were coated with thin layers of oxide. The spaces between metal grains may have been permeated by salt carrying tracer, and the surface oxide may have adsorbed large quantities of tracer if it did not dissolve fully in the melt. The salt did dissolve platinum metal of the container which separated as a gray colloid on cooling. Its proper treatment in the analysis and calculations is therefore uncertain. The study of the surface layers of the solid calcium and magnesium was never completely satisfying, although no large error is necessarily attached. With the possible exception of manganese, the experimental results selected as best values for the later discussion are probably close to the best obtainable by this general method, which is intrinsically of low precision.

Interpretation of Results in Terms of Equilibrium Constants.— Returning to the interpretation of results, it should be emphasized that because of the character of the liquid phases in these equilibria no single chemical equation can accurately represent any of them if the formulas of pure substances only are permitted. For simplicity,

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a type equation may be chosen and generally adhered to in thermodynamic treatments, as follows:

$$MX_2 + Pu = M + PuX_2$$

The actual salt, when M is uranium, is near to MX_3 in the vicinity of the melting points of the salts and near to MX_2 at the melting point of the metal. For cerium the relations are not yet fully determined, but MX_2 seems approximately correct, in some ranges at least. With the alkaline earths the composition is always between MX_2 and MX, generally closer to MX_2. The liquid metals in these cases also contain appreciable concentrations of dissolved salt. The equilibrium of plutonium metal with its halides has not yet been studied. It appears probable, however, that the salt phase will be between PuX_2 and PuX_3, perhaps closer to the latter in composition. For the present limited purposes, and with the present lack of precision, the equation above is adequate. Adopting it as the principal equilibrium and remembering that the Pu is dissolved at an extremely small mol fraction in solid or liquid M, and that PuX_2 is similarly dissolved in MX_2, the natural standard or reference states for the expression of thermodynamic data are the pure solid or liquid M, the pure liquid MX_2, and those hypothetical liquid states of Pu and PuX_2, respectively, that would make the activity of each equal to its mol fraction in the Henry's law range of solutions.

With these conditions met, the corresponding equilibrium constants, to be called K'_M and defined in terms of activities as $K'_M = (PuX_2)/(Pu)$ are numerically identical with the equilibrium

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ratios defined above, that is

$$(a) \qquad K'_M = k_m$$

The constants defined by (a), which will generally have to suffice for our comparisons, will be directly useful whenever the plutonium is present in dilute liquid or solid solution in the other metal and the two salts form a second dilute liquid solution phase.

It is, however, convenient when possible and more in line with the desired comparisons to take the pure liquid or solid plutonium and the pure liquid plutonium halide (PuX_2) as the reference states for this couple. If this is done, the corresponding equilibrium constant, to be called K, can be equal to k_M only if both solutions concerned in its definition are ideal or the solute plutonium and its halide have identical constants in Henry's law.

Concerning these equations, it would seem that deviations from Raoult's law must appear in the salt phase but that these will not be so great that they cannot be neglected in considerations like these. In the metal phase, on the other hand, Henry's law constants of the order of 10^3 or 10^{-3} instead of the ideal value unity of Raoult's law may well be met. If this analysis is correct, a closer approximation may be made, retaining all the original simplifying assumptions but writing

$$(b) \qquad K = k_M / k'_M$$

in which k'_M is the Henry's law constant of the tracer metal in the solid or liquid metal M. Notice that if the metals show negative

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deviations from Raoult's law (or tend toward compound formation), the measured k_M will be smaller than the desired K, while for metals that deviate positively (tend toward immiscibility) the measured constant is larger than the desired.

It is perhaps well to call attention to the fact that the values of K'_M apply only in the indicated solvent metal M, and are not necessarily "cross-comparable" as are the values of K when they can be obtained. This is a serious limitation in use. But for systems in which the tracer metal is quite soluble in the test metal M, these constants may actually be more convenient than others. If the plutonium is little soluble in M, the value of K above is more useful and has the advantage of independence of the particular system. Where the solubility is known, k'_M is determinable and K can be obtained from (b).

Discussion and Comment.-- Let us now examine Table III-14 in the light of the above points; first, with respect to K'_M and the strength of the plutonium couple involving the dissolved reference states.

It is found (2) and (3) that plutonium dissolved in uranium is a stronger reducing agent than the uranium at 1140°C. and also at 1000°C. Line (4) shows that thorium dissolved in uranium is within experimental uncertainty equivalent to uranium. Line (5) shows the cerium couple somewhat stronger than plutonium dissolved in cerium. The presence of iron in the cerium metal to the extent of several per cent without doubt has lowered k_M. Within the uncertainties, cerium and plutonium are therefore probably equal. Lead, as expected, is much weaker than plutonium, no doubt more so than indicated. Manganese is too uncertain

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to include in this discussion.

Among the alkaline earth metals the following points stand out. The liquid magnesium couple is weaker than the plutonium in it, as indicated by the experiments (9) to (11) and (13) and (14). This is true for all the halides tested. The variations among the different pure halides is in the direction anticipated. For solid magnesium at lower temperatures, near equality is found. The values of K_{Mg} with uranium tracer, (12) and (15), are in qualitative agreement with the direct comparison of plutonium and uranium, since they are smaller than the similar values with plutonium tracer. It is of some interest that the variation in solvent and solute has not changed the Henry's constants enough to upset this conclusion. For calcium, the best evidence (16) to (21), is that for the solid metal near 800°C., k_M is less than unity and calcium is the stronger reductant. For the liquid at 900°C., the two couples are nearly equal in strength, k_M being 0.85. Solid strontium at 708°C. and the liquid at 815°C. give constants of about 1/8 to 1/4, but with barium liquid near 900°C., (25) to (29), K'_M is again near unity.

Supplementary Observations.-- The above rather limited conclusions are all that can be drawn with certainty from the experiments listed in Table III-14. Some other illuminating results are, however, not included there. Thus, in all the experiments with alkaline earths that were done with liquid metals in iron containers, most of the plutonium was found in the iron at the end of the experiment. If equilibrium was established, this fact does not in any way affect the validity of k_M

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based on the plutonium in the alkaline earth metal. And it does permit, by analysis of the iron, assuming the distribution in it to be uniform, a determination of k_{Fe}, that is, the equilibrium ratio for plutonium dissolved in an iron phase, saturated with alkaline earth metal and therefore of unit activity of the alkaline earth. In this picture, the iron is not taking part in the reduction, but is acting as an extracting solvent, causing more complete reaction than would otherwise occur. From the behavior of the iron it seems quite certain that the Henry constant for plutonium in iron is less than unity. In other words, there are negative deviations from Raoult's law. The values of k_{Fe} set equal to K, the desired equilibrium constants, would then constitute minimum values of the latter. The values thus obtained for the magnesium system were from 5- to 20-fold smaller than k_{Mg}, but with strontium and barium were of the order of 10^4 fold lower. Such constants are more nearly of the magnitudes expected. It appears reasonable to assume that such values fix a lower limit of K, while K itself is below the measured k_M in each case.

As final points of some value in sizing up the tracer experiment situation, the results of a few experiments on decigram or centigram scale equilibria of magnesium and barium with uranium and the halides may be cited. Strips of uranium heated for 3 hours at 760°C. with liquid magnesium in an iron crucible, and magnesium heated in uranium in another experiment, with $MgCl_2$ alone and with UCl_3 present to start, gave values of 7.2 and 8.5 for K'_{Mg}, which may be compared with 7.5 from the tracer experiments (12). The solubility of uranium in magnesium is

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known approximately. The mol fraction of uranium in the saturated solution is about 0.002, giving a Henry's law constant of 500 and by (b) lowering K by this factor to about 1.6×10^{-2}. Three similar experiments with barium in uranium capsules at 906°C. gave K' equal to 0.0008, 0.014 and 0.0010, respectively. No Henry's law constant is known in this case. But if the data of (3) for plutonium in uranium at 1000°C. gives a fair comparison in this range, the above values of K' should be increased by a factor of at least 40 for comparison with the plutonium tracer results in the barium system. We would then have 0.03, 0.6 and 0.04 to compare (27) to (29) with values of 0.3, 1.1 and 1.1.

On the whole, such cross checks as have been made substantiate qualitatively the reliability of the experiments. It appears also that the values of K for the alkaline earths will prove to be well below unity, but not as far below as would generally be anticipated. The "sub-halide" equilibria change the reducing powers as compared with the normal halides, to which the only available free energy data apply, so that these equilibrium constants may remain for some time the only available quantitative estimates of the affinities concerned. Their usefulness will increase when the corresponding solubilities of plutonium in the metals become known.

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ELECTRONIC STRUCTURE OF PLUTONIUM

Inferences from Chemical and Physical Properties

Plutonium is the eighth element in the seventh period of the Periodic Table. The correlation of its chemical properties with its atomic structure can best be accomplished by considering it together with a number of the other elements in the seventh period (elements 89 to 94) in a discussion involving the chemical and physical properties of these elements.

Evidence for a "Rare Earth Group" in the Seventh Period.-- It seems very probable that some sort of a transition group should begin in the neighborhood of these elements. The elements 90 to 94 lie in corresponding positions just below the sixth period transition elements Hf to Os (atomic numbers 72 to 76) in which the 5d shell is being filled. The transition elements Hf to Os are quite similar in their chemical properties to the corresponding 4d transition elements in the fifth period (Zr to Ru) (atomic numbers 40 to 44). Although the first members ($_{90}$Th, $_{91}$Pa) of the group 90 to 94 show a great resemblance in chemical properties to the first members ($_{72}$Hf, $_{73}$Ta) in the 5d transition series and to the first members ($_{40}$Zr, $_{41}$Cb) in the 4d transition series, the later members ($_{93}$Np, $_{94}$Pu) show practically no resemblance to $_{75}$Re and $_{76}$Os and to 43 and $_{44}$Ru. Neptunium and Pu are much more electropositive in character than the noble elements Re, 43, Os and Ru. There is no evidence for a volatile plutonium tetroxide, in contrast

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with the volatile osmium and ruthenium tetroxides, and there is no evidence at all for an oxidation number of eight in plutonium. Thus, it seems certain that the transition in the elements 89 to 94 does not involve the simple filling of the 6d shell.

On the other hand, the chemical properties of Np and Pu are very similar to those of U and Th and are such as to suggest that the 5f shell is being filled and that we are dealing with another rare earth series similar to the well known "lanthanide" series, $_{57}La$ to $_{71}Lu$ (in which the 4f shell becomes filled). Such a series has been predicted a number of times on the basis of electronic structure considerations. There has been some uncertainty in these predictions with regard to the starting point of this series; the two principal choices have been between a "thoride" and a "uranide" series. From the standpoint of the chemical properties of $_{90}Th$, $_{91}Pa$, and $_{92}U$ considered alone, the evidence for such a series was not strong. However, with the discovery of Np and Pu, and the observation of the marked similarity of these elements to U and Th in chemical properties, the chemical evidence for a rare earth-like series has become very strong.

Hypothesis of an "Actinide" Series.-- An attractive hypothesis is that this rare earth-like series begins with Ac in the same sense that the "lanthanide" series begins with La. On this basis it might be termed the "actinide" series, and the first 5f electron might appear in Th. Thus, the ground state of Th might have the structure $5f^{1}6d7s^{2}$ beyond the radon core. With an "actinide" series, U would have the

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electron configuration $5f^3 6d 7s^2$, Np the configuration $5f^4 6d 7s^2$, and Pu the configuration $5f^5 6d 7s^2$.

It is very interesting to note that a preliminary analysis of the spectrum of neutral U atoms has given the result that the electron configuration of the lowest state of U is $5f^3 6d 7s^2$ (with the term symbol $^5L_6$), which supports the above view. Spectroscopic evidence that thorium possesses a ground state analogous to that of cerium also indicates that the characteristic configuration for uranium could involve three 5f electrons. Other observations, made on the Th(II) spectrum, indicate the presence of a 5f electron in this atom. Study of the X-ray data for Ra, Th and U lead to energy level diagrams which indicate that the 5f levels lie lower than the 6d levels and that the 5f shell begins to fill at thorium.

Correlation of Properties with the "Actinide" Hypothesis.-- The persistence of the (IV) oxidation state through the elements Th, U, Np and Pu is certainly good evidence that electrons are going into the 5f shell. The observation of the isomorphism of the compounds ThO_2, UO_2, NpO_2 and PuO_2, together with the observation of a regular decrease in radius of the metallic ion in these oxides in the anticipated manner, is also good evidence that the electrons are going into the 5f shell. A number of other crystallographic observations lend support to this view.

There are other points of evidence, such as (1) magnetic susceptibility measurements on U and Pu, (2) the sharpness of the optical

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absorption in aqueous solutions of U and Pu, and (3) evidence for organic complexes of U(IV) and Pu(IV) in which these elements have a coordination number of eight, which should also be considered. The magnetic susceptibility measurements on U(III), U(IV) and compounds of plutonium have shown that these are paramagnetic but have not lead to conclusive results with respect to the position of the electrons. However, the simplest qualitative explanation of the magnetic susceptibilities of Pu(III), Pu(IV) and Pu(VI) lies in the assumption that there are five 5f electrons in Pu(III) which are successively removed as one goes to the higher oxidation states. The sharpness of the absorption bands in solutions of uranium and plutonium compounds suggests 5f electrons. However, the nature of some of these absorption bands changes in some cases when different complex ions are formed to an extent which is greater than has been observed in the case of the 4f electron series. The evidence for organic complexes of U(IV) and Pu(IV) in which these elements have a coordination number of eight might indicate that the 6d, 7s and 7p orbitals are available, and hence might lend support to the view that the electrons are in the 5f orbitals. Since the energy of binding of the 5f and 6d electrons are so close to being the same, it may often be the case that changes in environment and state of chemical combination play a dominant role in determining the positions of the electrons with respect to these two orbitals.

All in all, it seems probable from these lines of evidence that the compounds of U and Pu (and Np) have electrons in the 5f shell;

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however, it is not possible to deduce from the chemical evidence whether or not U is the first element in the series for which this is the case. It would be consistent with this evidence for Th and Pa compounds to have no electrons in the 5f shell and for U compounds to have three electrons in this shell.

On the basis of an "actinide" series, the characteristic oxidation number for the series is III. The characteristic oxidation state of (IV) demonstrated by thorium is then analogous to the (IV) oxidation state of cerium. From the behavior of uranium, neptunium and plutonium, it must be deduced that as many as three of the assumed 5f electrons are fairly readily given up so that the failure of thorium to demonstrate an oxidation state of (III) is accounted for. The oxidation state of (IV) for uranium could then be considered analogous to the thorium(IV) structure.

The tendency in plutonium to stabilize the oxidation states of (IV) and (III) over the (VI) may perhaps find its explanation in a phenomenon already known in the lanthanide series. Gadolinium, with seven electrons in the 4f shell, has an extremely stable (III) oxidation state, corresponding to the stable configuration of $4f^7$. Europium, the element before gadolinium, attains a similar stable configuration by moving the 5d electron present in gadolinium to the 4f shell, giving it seven 4f electrons. Because of this configuration, europium possesses a stable oxidation state of (II) in addition to the characteristic state of (III). Similarly, terbium, the element beyond

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gadolinium, possesses an oxidation state of (IV) which brings it to the stable (III) gadolinium structure. In the case of plutonium, whose ground state as mentioned above might be considered on the "actinide" hypothesis to be $5f^5 6d 7s^2$, there may be a tendency to stabilize the electrons in the 5f shell so that removal of three 5f electrons, necessary to reach the oxidation state of (VI), is more difficult than for uranium. In plutonium the (III) state is relatively stable. Continuing this argument, it would be expected that element 95 should possess an oxidation state of (II) which is fairly stable, by keeping seven of its nine orbital electrons in the 5f shell. It should be quite difficult or impossible to oxidize this element to the (VI) state, and the characteristic oxidation state may be expected to be (III). Element 96 should exhibit an oxidation state of (III) almost exclusively.

As suggested earlier, it may become somewhat of an academic matter to assign electrons to the 5f or 6d shells as the energy necessary for the shift from one shell to the other may be within the range of chemical binding energies. The electron configuration may differ from compound to compound of an element or even with the physical state of a given compound. This shifting of electron configuration would probably be most pronounced with the middle members of the series, that is, uranium, neptunium and plutonium. Since the energy difference between the 5f or 6d shells is rather small and since the resonance effects should be rather large, the latter may predominate in determining which energy level lies lowest.

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Emission Spectrum of Plutonium.-- The emission spectrum of plutonium is, of course, too complex to be of any value at present in drawing conclusions as to the electronic structure of plutonium. Two photographs of the spectrum have been made using spark excitation; the first was taken with a 20 microgram, and the second with a 0.5 mg. sample. A qualitative estimate of the relative intensities of the lines was made using a scale from (0) to (10), with (0) representing the faintest lines which could be distinguished. Wave lengths with relative intensities from (1) to (1) inclusive are listed in Table III-15. Over 200 observed lines of intensity (0) are not listed in the Table. Lines marked (p) were found in both photographs, and those marked with an asterisk were also found in the second order. A possible band head is indicated by (bh), a hazy line by (h), and a very hazy line by (vh).

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Table III-15. The Emission Spectrum of Plutonium

Å	I	Å	I	Å	I
2611.74	1	2811.26	2	2906.88	3
12.80	1	15.78	2	09.47	1
14.85	1	16.41	1	10.43	8
31.23p	1	18.22	1h	11.50	1
58.47	2	22.93	5	12.50	2
61.10	1	26.36	1	13.79	1
62.58	1h	27.46	1	14.17	1
64.54	1vh	33.26	4	14.82	3
68.35	1	34.93	2	15.69	5
68.69	1	35.70Cr ?	8	18.10	8
69.71	1	38.73	1	18.84	1
70.37	1	40.57	3	19.97	2
74.74	1	42.72	2	21.83	3
90.75	1	47.22	1	23.02	4
94.46	1	49.29	1	23.70	1
2708.27	1	50.12	1	25.26*	7
28.15	1	51.20	3	26.53*	5
29.53	1	52.95	3	28.14*	6
30.76	1	56.17	2	29.37	6
44.21	1	57.06	5	30.82	2
46.97p	2	59.19	1	32.17	2
48.51Cd ?	1	60.03p	5	33.22	3bh?
54.76	2	61.16	1h	36.36	4h
58.64	1	62.57	4h	37.52	2
60.31	1	66.42	3	38.90	8
71.04	1	66.96	3	41.27	6
76.36	2	67.63	1	43.04	2
79.90	1	69.05	4	49.85p	7
81.41	3	70.05	2	51.64p	3h
84.50	5	72.20	2h	54.33p	7
85.64	2	74.79	2	56.30	2h
87.31	2	76.56	2h	63.40	2
89.10	3	79.96	2	64.70p*	8
93.32	1	85.40	3vh	66.09p	1
94.64	1	86.83	2h	66.80p	2
97.16	1	87.79	1h	67.58	2
98.76	1	90.72	2	68.98p*	5
2800.40	1	91.71	3	69.91	1
01.61	1	92.64	4	70.52p	3
03.98	2	94.54	4h	72.51p*	10
05.21	1	95.67	2	73.45	2
05.48	1	97.90Bi ?	5	78.03*	7
06.06	2	99.62	3	78.49p*	9
06.37	1	2900.80	2h	80.27p*	10
06.93	1	03.19	1	81.26	3
08.38	4	04.17	3	82.65	1
10.38	2	04.87*	6	84.24	1

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Table III-15 - Continued

Å	I	Å	I	Å	I
2984.98	1	3057.64*	2	3236.82	1
87.12p	6	58.41*	4	41.37	8
88.21p*	10	60.18*	4	42.04	7
90.09	2	61.76	4	45.23	6
91.55p	8h	69.25p*	9	53.75	4
92.60	2	74.65*	3	54.58	3
94.06p	10	75.47	1	61.20Cd ?	3
96.46p	9	76.01	1	63.17	2
98.46p	3	79.77	2	64.21	3
3000.62p*	10	84.63	4	71.26	4
02.43	2h	3105.28	3	79.17	1
04.86p	3	09.30p	2	87.83	1
05.46	2	18.75	2	98.42	8
07.38	5	21.18	2	3302.52	3
09.14Sn ?p*	6	37.52	2	12.61	8
09.83*	6	65.52	2	13.57	2
12.88	1	67.58	1	14.69	1
13.58	2	71.44	1	15.38	7
14.54	3	73.12	2h	16.27	2h
15.05	3	74.68	3	21.76	2
15.97	2	76.67	1	23.83	8
18.21	4	79.71	6	24.73	4
19.50*	4	82.36	4	27.58	2
21.14p*	8	83.55	1h	74.61	1
23.42p*	7	84.49	1	77.34	8
25.96p	4	85.65	4	79.41	1
28.84	6	96.34	1h	83.99	1
29.89p	7	97.85	2	87.08	1h
31.42	8	98.48*	6	87.91	2h
32.47p	8	3200.39	5	89.30	6
33.97Sn ? p	4	01.59	5h	90.13	4
35.26	1	03.07	6vh	91.40	8
38.50p	4h	04.75	3h	92.20	3h
39.23	3h	06.98	4	92.92	2h
41.51	3	11.26	1h	93.97	1
42.67*	5	13.73	1h	94.39	1
43.05p*	5	15.33	1	97.36	9
46.36	7	16.21	3	3401.03p	10
47.42	3	17.21	2	07.36	1
48.25	1	18.18	1	10.12	4vh
49.01	1	19.10	3	12.41	4
51.11	5	21.01*	7	14.23	5
52.16	2	21.73*	8	15.02	1
53.16*	8	22.65	1	16.74	2
53.89	1h	29.66	2vh	17.96	1
55.24	3vh	31.89	9	18.91p	10
55.86	3vh	32.61Sb ?	4	21.30Pd ?	3
56.81	3	34.74	5	22.67	2

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Table III-15 - Continued

Å	I	Å	I	Å	I
3424.12p	8	3540.76*	7	3645.77p	8
24.61	8	42.03	2h	47.92p	8
25.45p	10	50.63	1h	49.20p	6
26.33	6	78.05	1	50.43	4
28.24	1	78.62	4	51.40p	8
29.27	1	79.45	2	52.23	2
30.29	1	85.92p*	10	57.70Rh ?	2
31.17	1	88.05	2	59.39p	5
32.90	4	89.52	1	60.62p	2
34.28	2	90.21	3	61.87	1
35.00Rh ?	8	91.68p	2	63.82	3
39.42	1	92.53	2	64.49	1
42.26	4vh	93.34	4h	67.31	2
44.04	2	94.16	3h	67.88	7
44.77	2	95.19	2	68.83	2
45.81	1vh	96.01	1	70.07	3
47.16	1vh	96.24	2	73.35	1vh
49.10	4	3600.48p	8	74.88	7
53.02	1	02.79p	1h	78.41	1h
53.79Co ?	1	03.72p	8h	78.77	1h
55.26	6	05.02	1	79.65	5
56.21	2	05.98p	8	80.52	3
57.05	1	07.22	4h	81.98	2vh
58.88	6	07.80	4h	82.92	8
60.33Re ?	2h	08.75p	4	85.46	3
60.81	3h	09.58Pd ? p	4	88.65	2h
61.89	2	12.36	2vh	89.82	2
62.67*	6	15.05	1	90.44p	6
63.53*	3	15.62	3	91.34p	3
65.02p*	10	16.09	2	93.68p	5
69.22*	10	16.90	1	95.21p	5
70.43	1h	17.78	1	96.77	1
71.00	1h	19.26p	3	99.35p	5
73.67p*	10	21.50p	8	3714.01	2h
78.24	2h	23.05	2	14.78	2
79.06	1	25.49	6h	18.69p	10
79.88	2	28.70	3	20.32p	7
83.19p*	7	29.73	2	21.50p	8
88.17	2	30.29	1	24.09	1
91.31	1h	31.96 to 32.77 p	10vh,bh?	25.99p	10
94.45	3			26.71p	10
96.35	2	34.97Pd ?	2	32.04p	8
97.25*	4	35.87p	8	32.46	4
3504.89	2	36.47p	8	36.17	2
06.88	1	38.07	3	37.30p	2h
15.25	1	38.65	1	39.24p	7
16.73Pd ?	2	39.90	3h	58.19p	2
33.33	3	44.24	1h	58.64p	4

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Table III-15 - Continued

Å	I	Å	I	Å	I
3761.13	2	3866.75	7	4048.83p	4
63.05	3	71.86	4	58.71	6h
64.12	3h	72.35	4	64.70p	9
65.05	3h	74.23	4	65.67	2
67.34	2	74.92	7	66.80p	9
70.21p	7	76.62	1	71.30	2
70.98	1	78.47p	2	71.90	2
71.65	7	3906.24	10h	74.22	6h
73.44p	9	45.42	1h	74.58	8
76.00p	9h	46.93	4	78.09	8
3806.18	1	49.19	10h	84.39	1
07.34	3	50.31	2	88.85	8
08.57	2	51.60	4	97.76	7
09.61	3h	52.97p	8	4101.02	5
10.52	9	56.46	1h	02.04	2
12.02	5	57.56	2h	03.28	1
12.67	7	58.93p	8	03.86	6
15.26	8	62.68	3	06.00	8
24.24p	7	65.44p	3	07.34	6
26.16p	4	67.24	2	08.52	3h
27.66	6	70.11	2	12.54	2
28.00	1	71.52p	3	13.20	2
29.50Mg ?	6	72.18p	9	14.99	1
32.28Mg ?	4h	72.96	1	16.54p	7
33.61	3	75.40p	9	17.33	1
35.52	6	75.82p	6	36.76	9
36.12	6	79.83	1	46.39	2h
37.00	8	80.34	6	46.76	1h
39.98	1	84.13	3	49.16	2h
40.79	8	85.48	9	50.00	4
41.45	2	89.76p	9	55.98	1
42.21	5	92.24	6	59.65	2vh
43.49	1	96.08	4	60.68	1
45.80	3h	4000.25	2	67.76p	10
46.72	10	01.94	2	69.78	1
48.11	1	02.59	4	75.52	1
49.01	2	04.64	1	78.33p	2
50.16	6	06.37	7	90.02	8
51.19p	9	07.73	1	90.83	5
51.86	7	10.56	2	96.21p	9
52.70p	8	14.62	1	4203.19	1vh
53.17	2h	15.74p	6	04.79	3
54.08	1	19.22	1	05.60	2
58.42	2	32.92	1	06.42	2vh
59.17	3	34.93	4	08.26	8
61.12	9	35.80	6	08.77	7
62.44	4	37.20	4	12.07	7
64.96	9h	39.38p	6	15.26	5

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Table III-15 - Continued

Å	I	Å	I	Å	I
4216.39	9	4406.80	7	4823.00	6
19.01	5	19.42p	8	42.40	1vh
29.79	8	21.73	2vh	47.49	1vh
30.76	4h	35.53p	1	50.07	3
33.62	6	37.26	2	64.75	1h
37.85	6	40.24	2	84.30	1
49.64	3	41.63p	6	86.83	1vh
51.38	2	48.27	2	87.30	1vh
54.77p	4	56.72	3	94.42	1vh
55.93p	6	59.12	1	96.73	2
73.31p	8	4502.23	1	4904.71	2
79.67	1	04.90p	7	27.44	2
80.18	8	11.13In ?	1h	37.98	1h
81.12	2	33.59	1	45.25	1
82.10	1	36.05p	10	57.40	1
83.80p	7	54.15Ba ?	2h	69.83	1vh
85.88	1	79.58	1	70.88	1
87.48	1	4610.59	2	82.59	1
89.08p	9	15.42	1	5023.31	1
99.46	6	19.00	1	38.04	1
4307.18	4h	27.43	7	57.33	1
09.73	1	39.50	4	78.11	2vh
11.92	1vh	55.26	1	5103.13	1h
13.33	2h	56.60	1	69.93	1
14.43p	6h	57.42	4	94.00	2
16.68	2h	64.23	6	5209.80	2
18.76	1	71.00	2h	21.41	1
20.29	2h	73.13	3h	68.05	1
20.81	2h	80.23	3	88.62	1
22.04	1	89.52	6	5423.26	4
24.35	4	90.72	1vh	5767.96	1
26.36	2h	92.10	3	5818.46	1
30.65p	10h	93.93	1	57.02	4
36.09	6	98.76	2	92.94	2
37.19	9	4701.27	7	6192.72	1h
41.48	10	11.32	1	6321.87	1h
52.62p	10	22.81	2	23.81	1h
57.96p	7	26.41	2	24.75	1
71.42	2	31.22	3h	80.69	3h
79.81p	5	48.84	1	6417.39	1
81.02	4	67.22	8		
83.46p	7	68.62	1vh		
85.40	9	81.01	2vh		
92.80	2	94.57Cl ?	10		
93.92p	9	4802.09	1		
96.35	9	09.05	1		
4404.17	1h	10.05Cl ?	9		
04.95	7	19.27Cl ?	8		

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CHAPTER IV

THE CRYSTAL STRUCTURE OF PLUTONIUM AND ITS COMPOUNDS

This chapter gives a survey of results obtained through X-ray diffraction studies of plutonium and its compounds. The crystal structure data for individual plutonium compounds are summarized in the next section, while the last section is devoted to a discussion of the general conclusions which can be drawn regarding the crystal chemistry of plutonium. The summary of results given in the next section of this chapter is somewhat less detailed than that which appeared in a recent Project publication which gives a fairly extensive bibliography of reports and memoranda containing the original results.

The X-ray diffraction studies of plutonium compounds were carried out under such unusual conditions that the customary methods of approach in crystal structure investigations could not be followed.

The first problem which presented itself was that of obtaining satisfactory X-ray diffraction patterns of powder samples weighing as little as ten micrograms. It was found that only comparatively small improvements in existing experimental technique were needed in order to overcome this difficulty.

When, under normal circumstances, a crystal structure investigation is undertaken, both the chemical identity and the density of the substance under examination are known as a matter of course. Because of the small amounts of material with which the chemists had to work, information about the chemical composition and density was not available for plutonium preparations, and this fact represented a most serious

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difficulty as regards the interpretation of the X-ray diffraction patterns. The method of preparation was, of course, known. However, because of the many unforeseen difficulties which arise in the course of chemical preparations on the microscale, and because the chemistry of plutonium was largely unknown, a knowledge of the method of preparation was, as a rule, not sufficient as a basis for correctly guessing which compound would be present in a given preparation. Indeed, the X-ray diffraction studies have demonstrated that most samples contained more than one phase.

It is clear that the interpretation of the X-ray diffraction patterns under these conditions had to proceed along highly unorthodox lines. A great many novel methods of approach were used in the course of these investigations. A description of these methods would, however, be too technical and too lengthy to be given here. As a rule it was not possible first to identify the phases observed in the diffraction pattern and then to find their crystal structure. Indeed, these two steps in the investigation followed in general in the reverse order. In most cases a partial determination of the crystal structure was carried out first, and then the phase in question was identified on the basis of the information so gained.

CRYSTAL STRUCTURE DATA FOR PLUTONIUM AND ITS COMPOUNDS

Plutonium compounds which have been definitely identified and for which lattice dimensions and partial or complete crystal structures have been determined are:

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Plutonyl Compounds:	$NaPuO_2(Ac)_3$
Tetravalent Compounds:	PuO_2
	PuF_4
	$PuF_4 \cdot 2 \cdot 5H_2O$
	K_2PuF_6
Trivalent Compounds:	Pu_2O_3
	PuF_3 PuOF
	$PuCl_3$ PuOCl
	$PuBr_3$ PuOBr
	PuI_3 PuOI
	$PuPO_4 \cdot 0\text{-}0.5H_2O$
Metallic-type Compounds:	Pu
	PuO
	PuN
	PuC
	$PuSi_2$

The following compounds have definitely been identified, although their lattice dimensions have not been determined:

$(NH_4)_2Pu(NO_3)_6$, $Pu_3(PO_4)_4 \cdot x\ H_2O$, $Pu(C_2O_4)_2 \cdot x\ H_2O$,

$PuCl_3 \cdot H_2O$, $PuCl_3 \cdot 6\ H_2O$, $PuBr_3 \cdot 6\ H_2O$, β- Pu.

There are some substances for which lattice dimensions are known, but for which the chemical identity is as yet uncertain. The tentatively assigned formulas of these substances are:

$PuOF_2 \cdot 2\ H_2O$??, $Pu(F_{0.85}Cl_{0.15})_3$?, Pu_2C_3 ??, PuS ?

Of the plutonium compounds listed above, $PuBr_3$ and $PuCl_3 \cdot H_2O$ were first definitely identified by means of chemical analysis. PuF_3 and

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PuOF were first identified as PuF_3 or $PuOF_2$ and PuOF or $PuF_{2.3}$, respectively, by X-ray diffraction methods, but subsequent chemical analysis distinguished between the proffered alternatives. For $PuCl_3 \cdot 6\ H_2O$, simultaneous and independent identifications were made by chemical and X-ray methods. All the other compounds given in the list were first identified by crystal structure methods, and the identification has in some instances been confirmed by subsequent chemical analysis.

Plutonyl Compounds

$NaPuO_2\ (C_2H_3O_2)_3$.— This compound is cubic. The unit cell contains four molecules and has dimensions

$$a = 10.643 \pm .002A.$$

The calculated density is $\rho = 2.578$.

The space group is P23 (T^4).

The metal positions have been determined.

Isomorphous compounds are:

$NaUO_2\ (C_2H_3O_2)_3$ and $NaNpO_2(C_2H_3O_2)_3$.

Tetravalent Compounds of Plutonium

PuO_2.— The dioxide is cubic and has the fluorite type of structure. The lattice constant is

$$a = 5.386 \pm .002A$$

and the calculated density is $\rho = 11.44$.

Isomorphous dioxides are: ThO_2, UO_2, NpO_2, CeO_2, PrO_2, HfO_2, ZrO_2.

PuF_4.— The tetrafluoride is monoclinic with 12 molecules per unit cell. The lattice dimensions are:

$$a_1 = 12.6 \pm 0.1A \qquad a_2 = 10.6 \pm 0.1A$$

$$a_3 = 8.3 \pm 0.1A \qquad \alpha_2 = 126^\circ \pm 1^\circ$$

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The calculated density is $\rho = 7.0$.

The space group is C2/c (C_{2h}^6).

The positions of the metal atoms have been deduced.

Isomorphous tetrafluorides are:

ThF_4, green UF_4, CeF_4, HfF_4, ZrF_4.

$PuF_4 \cdot 2.5\ H_2O$.— The symmetry is orthorhombic. The unit cell contains eight molecules and has dimensions

$$a_1 = 12.63 \pm .05A, \quad a_2 = 11.01 \pm .05A, \quad a_3 = 6.98 \pm .05A$$

The calculated density is $\rho = 4.89$.

The space group is Pn a m (D_{2h}^{16}).

The positions of the metal atoms have been determined.

The corresponding uranium compound is isomorphous.

K_2PuF_6.— This compound is rhombohedral. The face-centered rhombohedral cell has dimensions

$$a = 5.856 \pm .008A \qquad \alpha = 89^\circ 22'.$$

There are 4/3 molecules in this cell and the calculated density is $\rho = 4.71$.

The compound has a slightly deformed CaF_2 - type of structure.

Isomorphous compounds are: K_2ThF_6 and K_2CeF_6.

$Pu_3(PO_4)_4 \cdot x\ H_2O$.— The X-ray diffraction pattern of this substance has not been interpreted, but proves isomorphism with the analogous compounds of thorium and cerium.

$Pu(C_2O_4)_2 \cdot x\ H_2O$.— The diffraction pattern of this compound is too poor to permit interpretation.

Isomorphism with the corresponding uranium compound is, however, established.

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$(NH_4)_2Pu(NO_3)_6$.— This salt is isomorphous with the analogous compounds of thorium and cerium; but lattice constants have not been deduced.

$PuOF_2 \cdot 2\ H_2O$??.— This substance is isomorphous with a uranium compound prepared by a method which, according to the literature, should yield $UOF_2 \cdot 2\ H_2O$.

The compound has a disordered structure, possibly of tetragonal symmetry. There is a cubic pseudo-cell of lattice constant

$$a = 2.808 \pm .010A.$$

If the assigned formula is correct, there is 1/4 molecule per pseudo-cell corresponding to a calculated density of $\rho = 5.10$.

Trivalent Plutonium Compounds

$Pu_2O_3 - Pu_4O_7$.— This substance is cubic body-centered with 32 metal atoms per unit cell.

The lattice constant appears to vary from one preparation to another

$$a = 10.95 - 11.01A.$$

There is a face-centered pseudo-lattice with constant a/2.

This phase was formerly thought to be Pu_2O_3. It is now believed that a complete reduction to Pu_2O_3 may not have been achieved.

The structure is, however, essentially that of the modification C of the rare earth sesqui-oxides.

PuF_3.— The trifluoride is hexagonal. The unit cell containing two molecules has dimensions

$$a_1 = 4.087 \pm .001A, \qquad a_3 = 7.240 \pm .001A.$$

The calculated density is $\rho = 9.32$.

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The trifluoride has the LaF_3 - type of structure.

Isomorphous trifluorides are:

UF_3, LaF_3, CeF_3, PrF_3, NdF_3, SmF_3, $(Th, Pb)F_3$, $(Th, Ca)F_3$.

PuF_3 forms a complete series of solid solutions with LaF_3.

PuOF.— PuOF is cubic and has the CaF_2 type of structure. The lattice constant is

$$a = 5.70 \pm .01A$$

and the calculated density is $\rho = 9.76$.

It is probable that PuOF may take up as much as 25% PuF_3 in solid solution.

The only known isomorphous oxy-fluoride is LaOF.

$PuCl_3$, $Pu(Br_{0.8}Cl_{0.2})_3$, $Pu(F_{0.85}Cl_{0.15})_3$?.— The trichloride is hexagonal with two molecules per unit cell. The lattice constants are:

$$a_1 = 7.380 \pm .001A, \qquad a_3 = 4.238 \pm .001A.$$

The calculated density is $\rho = 5.70$.

The space group is $C6_3/m$. The complete structure, which is of a new type, has been determined.

A mixed crystal of the trichloride and the tribromide with an estimated composition $Pu(Br_{0.8}Cl_{0.2})_3$ and a substance believed to be $Pu(F_{0.85}Cl_{0.15})_3$ both have been shown to be isomorphous with $PuCl_3$. The lattice constants of these substances are:

	a_1	a_3
$Pu(F_{0.85}Cl_{0.15})_3$	$6.12 \pm .02A$	$3.75 \pm .02A$
$Pu(Br_{0.8}Cl_{0.2})_3$	$7.806 \pm .018$	$4.302 \pm .004$

Isomorphous trihalides are:

UCl_3, UBr_3, $LaCl_3$, $LaBr_3$, $CeCl_3$, $CeBr_3$, $PrCl_3$, $PrBr_3$, $NdCl_3$.

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It is of importance to note that $PuBr_3$, $NdBr_3$, $SmBr_3$ are not isomorphous with $PuCl_3$ in contrast to UBr_3 and $LaBr_3$ - $PrBr_3$.

$PuBr_3$ and PuI_3.-- These two compounds are orthorhombic and isomorphous with each other. The unit cells in which there are four molecules have dimensions

	a_1	a_2	a_3
$PuBr_3$	12.57 ± .05A	4.11 ± .03A	9.13 ± .04A
PuI_3	13.9 ± .1	4.29 ± .04	9.90 ± .10

The calculated density is 6.69 for $PuBr_3$ and 6.92 for PuI_3.

The space group is C c m m (D_{2h}^{17}).

The complete structure has been determined. It is of a new layer lattice type.

Isomorphous compounds are: UI_3, LaI_3, $NdBr_3$, $SmBr_3$.

$PuCl_3 \cdot H_2O$.-- The X-ray diffraction pattern of this compound has not been interpreted, and isomorphism with other substances has not been established.

$PuCl_3 \cdot 6\ H_2O$ and $PuBr_3 \cdot 6\ H_2O$.-- The X-ray diffraction patterns show these substances to be isomorphous with each other and with $NdCl_3 \cdot 6\ H_2O$. Lattice dimensions are not known.

PuOCl, PuOBr and PuOI.-- These three oxy-halides are isomorphous with one another and have the PbFCl - type of structure.

The tetragonal unit cells containing two molecules have dimensions

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	a_1	a_3
PuOCl	4.004 ± .002A	6.779 ± .010A
PuOBr	4.014 ± .004	7.556 ± .011
PuOI	4.034 ± .002	9.151 ± .015

The calculated densities are $\rho = 8.81$ for PuOCl, $\rho = 9.07$ for PuOBr and $\rho = 8.46$ for PuOI.

Isomorphous oxyhalides are: BiOCl, BiOBr, BiOI, LaOCl, LaOBr, LaOI, PrOCl, PrOBr, NdOCl, NdOBr, YOCl.

$PuPO_4 \cdot 0\text{-}0.5\ H_2O$.-- This compound is hexagonal. The unit cell containing three molecules has dimensions

$$a_1 = 6.99 \pm .01A, \qquad a_3 = 6.48A.$$

The value $a_3 = 6.48A$ given in the original report is now believed to be inaccurate and a redetermination is in progress. The calculated density, using $a_3 = 6.48A$, is $\rho = 6.04$.

The space group is C3, $2(D_3^4)$ or the enantiomorphic $C3_22(D_3^6)$. The complete structure has been determined.

The water present in the structure is of zeolithic type and most of it can be driven off without destruction of the lattice.

Isomorphous compounds are the α-forms of:

$$BiPO_4, \quad LaPO_4, \quad CePO_4, \quad NdPO_4, \quad YPO_4.$$

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Plutonium Metal and Compounds of Metallic Type

Alpha-Plutonium.-- Several diffraction patterns were obtained from rolled sheet and extruded wire specimens. All of these patterns were similar and indicated at least two phases present. The predominant phase at room temperature is isomorphous with the orthorhombic uranium structure. The lattice constants are: $a_o = 2.89A$

$b_o = 5.67$

$c_o = 4.81$

y = not determined

The density calculated from this structure is 20.0 gm. per cc. The best value of a measured density of the alpha modification is 19.8 gm.per cc.

Beta-Plutonium.-- A diffraction pattern of the beta modification was obtained at 150°C. The structure has as yet not been determined. A comparison of this pattern with that obtained at room temperature indicated that the second phase present at room temperature is retained Beta-plutonium. The density of Beta-plutonium as measured and extrapolated to room temperature is 17.8 gm. per cc.

Gamma-Plutonium (?).-- The face-centered cubic structure ($a_o = 4.60A$) so often observed in the early lithium reduced metal has again been observed in an aluminum alloy of 1.0 atomic per cent aluminum annealed at 330°C. and fast cooled. The density of the aluminum alloy (and of the early lithium reduced metal which was known to contain aluminum) has been measured as low as 15.8 gm. per cc. The calculated density of pure metal in the face-centered cubic modification is 16.2 gm. per cc.

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Diffraction patterns of several metal samples obtained in the early micro-scale reductions revealed a cubic close-packed structure. The lattice constants of these samples, which were believed to contain 5 per cent thorium, was

$$a = 4.61 \pm 0.03A$$

Assuming 5 per cent thorium, the calculated density for this form of pure plutonium extrapolates to 16.5 gm. per cc. It seems certain that these were samples of gamma-plutonium.

PuO.-- The monoxide, which now can be regarded as definitely identified, is cubic and has the NaCl - type of structure.

The lattice constant is

$$a = 4.948 \pm 0.002A$$

and the calculated density is $\rho = 13.95$.

PuN.-- The mononitride is cubic and has the NaCl - type of structure. The lattice constant is

$$a = 4.895 \pm 0.001A$$

and the calculated density is $\rho = 14.23$.

PuC.-- The monocarbide, like PuO and PuN, has the NaCl - type of structure. The lattice constant is

$$a = 4.910 \pm 0.005A$$

and the calculated density is $\rho = 13.99$.

Pu_2C_3 (?)-- The formula Pu_2C_3 is highly uncertain, as is also the information given below.

The symmetry may be cubic body-centered with a lattice constant

$$a = 8.11 \pm 0.01A$$

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If the assigned formula is correct, there would be eight molecules per unit cell corresponding to a calculated density of $\rho = 12.70$.

The space group may be $I\,\bar{4}3d$ (T_d^6).

$PuSi_2$.-- The disilicide is tetragonal with four molecules per unit cell. The lattice constants are:

$$a_1 = 3.97 \pm .01A, \qquad a_3 = 13.55 \pm .03A.$$

The calculated density is $\rho = 9.12$.

The space group is I 4/a m d (D_{4h}^{19}) and the complete structure has been determined.

PuS ?.-- The substance referred to as PuS ? is either simply BaO or PuS (possibly with some BaS in solid solution).

The substance has the NaCl - type of structure with lattice constant

$$a = 5.525 \pm .001A.$$

If the formula PuS is correct, the calculated density is $\rho = 10.60$.

X-ray diffraction methods cannot distinguish between the two alternative formulas.

At the present writing it seems likely that the substance is PuS (and not BaO) with 10% BaS in solid solution.

THE CRYSTAL CHEMISTRY OF PLUTONIUM

Valence States and Nature of Chemical Binding.-- The valence states +3, +4, +5 and +6 have definitely been established for plutonium. The +5 state is so far known only in solution, and hence it does not concern us.

The X-ray diffraction work has led to identification of the compound PuO. This should not be taken as evidence of a legitimate +2 state any more so than the compounds CeS, US, ThS, Th_2S_3 can be regarded as proofs

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of Ce^{+2}, U^{+2}, Th^{+2}, Th^{+3}. The reason for this opinion is that the binding in PuO, as in CeS, US, ThS, Th_2S_3, is of predominantly metallic type to which the usual valence rules do not apply.

The +6 state is the plutonyl state. The known hexavalent plutonium substances are in other words compounds of the radical $(PuO_2)^{+2}$. Whether or not true hexavalent compounds of plutonium exist is not known at present. Efforts to prepare PuF_6 have so far been unsuccessful. Certainly the Pu-O bonds within the plutonyl radical must be of covalent type. The limited amount of crystal structure data available for uranyl and plutonyl compounds indicate, however, that the bonds from plutonium and uranium to fluorine atoms and to other oxygen atoms may be regarded as predominantly ionic in character.

The crystal structures which have been found for tetravalent and trivalent compounds obey the general principles of ionic structures. Although the chemical bonds in these compounds undoubtedly must be regarded as of mixed ionic-covalent type, the crystal structure data show that the ionic character of the bonds predominates.

In the preceding section the compounds PuO, PuN, PuC, $PuSi_2$ have been grouped with the metal itself as metallic type compounds. This does not imply that the binding in these compounds is assumed to be of pure metallic character. It is probably more correct to say that a transition type between metallic and covalent bond is involved in these substances.

Plutonyl Compounds.-- There is unfortunately only one plutonyl compound for which X-ray diffraction patterns have been obtained and this is $Na(PuO_2)(Ac)_3$. The substance is isomorphous with the corresponding uranyl and neptunyl compounds.

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The values for the edge of the unit cube of the three substances are

	a
$Na(UO_2)(Ac)_3$	10.671 ± .001A
$Na(NpO_2)(Ac)_3$	10.659 ± .002
$Na(PuO_2)(Ac)_3$	10.643 ± .002

The space group and positions of the metal atoms have been found; but because of their small scattering power it is not possible to locate the light atoms. A complete structure has, it is true, been proposed for the uranyl compound (J. Fankuchen, Z. f. Krist, 91, 473 (1935)), but the size of the uranyl group is unreasonably large, so that the proposed structure cannot be accepted as more than approximately correct.

Space group considerations show that the $(XO_2)^{+2}$ group must be linear. A reasonable guess as to the size of the $(XO_2)^{+2}$ groups is

	X-O
$(UO_2)^{+2}$	1.85A
$(NpO_2)^{+2}$	1.84A
$(PuO_2)^{+2}$	1.82A

The small difference in the dimensions of the $(XO_2)^{+2}$ groups shows that complete isomorphism is to be expected between all plutonyl, neptunyl and uranyl compounds. Indeed, neptunium and uranium (apart from transplutonic elements) are the only crystal chemical stand-ins for plutonium in the +6 state.

The binding within the $(XO_2)^{+2}$ radical is certainly of covalent type. The close similarity between the three groups $(UO_2)^{+2}$, $(NpO_2)^{+2}$ and $(PuO_2)^{+2}$ accordingly cannot be explained unless the outer electronic system is the same in the three cases. As a consequence, there must be at least one

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5f - electron in neptunium and at least two 5f - electrons in plutonium.

It is to be hoped that the X-ray diffraction studies can be extended to many other plutonyl compounds. Plutonyl fluoride, PuO_2F_2, would be of particular interest.

Tetravalent Compounds.-- Crystal chemical similarity to Pu^{+4}, as evidenced by isomorphous compounds, is shown by the following tetravalent ions: Th^{+4}, U^{+4}, Np^{+4}, Ce^{+4}, Pr^{+4}, Hf^{+4} and Zr^{+4}. The compounds for which isomorphism has been established are indicated by crosses in Table IV-1.

Table IV-1. Isomorphism for Tetravalent Compounds

Compound	Th	U	Np	Ce	Pr	Hf	Zr
PuO_2	x	x	x	x	x	x	x
PuF_4	x	x		x		x	x
$PuF_4 \cdot 2.5\ H_2O$		x					
$PuOF_2 \cdot 2\ H_2O$?		x					
K_2PuF_6	x			x			
$Pu_3(PO_4)_4 \cdot x\ H_2O$	x			x			
$Pu(C_2O_4)_2 \cdot x\ H_2O$		x					
$(NH_4)_2Pu(NO_3)_6$	x			x			

The experimental data are as yet highly incomplete. It may safely be assumed that Pa^{+4} will have to be added to the list of ions closely related to Pu^{+4}. However, it can be stated with certainty that there are no other ions which are crystal chemically similar to Pu^{+4}. The ions Tb^{+4} and to a lesser extent Pb^{+4} should have been included, but there are so few compounds of these ions (and indeed also of Pr^{+4}) that they may well be omitted. The only ions which need to be considered as stand-ins for Pu^{+4} are thus

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Th^{+4}, Pa^{+4}, U^{+4}, Np^{+4}, Ce^{+4}, Hf^{+4}, Zr^{+4}.

Because of the incompleteness of available data, the number of entries in Table IV-1 cannot be taken as as indication of how closely related a given ion is to Pu^{+4}. In order to get information on this point, it becomes necessary to consider the relative sizes of the ions.

The radii of the ions concerned relative to that of Pu^{+4} have been deduced from the X-ray diffraction data. The results are shown in Table IV-2. The values given in parenthesis represent estimates. It should be stated that the radii given in Table IV-2 strictly speaking apply to oxygen and fluorine compounds.

Table IV-2. Radii of Tetravalent Ions Relative to the Radius of Pu^{+4}

Ion	$R_x - R_{Pu}$
Th^{+4}	+.09A
Pa^{+4}	(+.06)
U^{+4}	+.03
Np^{+4}	+.02
Ce^{+4}	+.01
Pr^{+4}	0
Tb^{+4}	(-.10)
Hf^{+4}	-.12
Zr^{+4}	-.13
Pb^{+4}	-.14

In order to predict interatomic distances, the absolute radius must be known and the proper corrections applied. The set of ionic radii deduced by V. M. Goldschmidt (Skr. Norske Vidensk. Akad. No. 288, 1926) is satisfactory for our purposes, although the accuracy can be increased by a more

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refined treatment (W. H. Zachariasen, Zeitschr. f.Krist.80,137 (1931)). In the Goldschmidt system only correction for coordination number is applied. The increase in interatomic distance for various coordination numbers relative to the value for coordination number six is

CN	Increase in per cent
12	7
9	4
8	3
4	-4

Using Goldschmidt's radius for F^{-1} of 1.33A and the value 1.40A for O^{-2} (in preference to Goldschmidt's value 1.32A), the ionic radii shown in Table IV-3 are obtained.

Table IV-3. Ionic Radii for Tetravalent Ions

Ion	Radius
Th^{+4}	0.97A
Pa^{+4}	0.94
U^{+4}	0.91
Np^{+4}	0.90
Ce^{+4}	0.89
Pu^{+4}	0.88
Pr^{+4}	0.88
Tb^{+4}	0.78
Hf^{+4}	0.76
Zr^{+4}	0.75
Pb^{+4}	0.74

Leaving for consideration only those elements which commonly form tetravalent compounds and those elements which are commonly available,

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we have the set Th^{+4}, U^{+4}, Ce^{+4}, Hf^{+4}, Zr^{+4}.

On the basis of the results given above, it can be stated that Ce^{+4} is a nearly perfect crystal chemical stand-in for Pu^{+4}. Also, U^{+4} is an excellent stand-in, but not quite as good as Ce^{+4}. Next in order of excellence as stand-ins for Pu^{+4} come Th^{+4}, Hf^{+4}, and Zr^{+4}.

Analogous compounds of Pu^{+4}, Ce^{+4} and U^{+4} will always have the same crystal structure (except in the very rare cases where the stability limit of the structure is crossed in going from one to another of these ions). Thorium compounds should in many cases be isomorphous with the corresponding plutonium compounds. Isomorphism between plutonium compounds and analogous compounds of Zr^{+4} and Hf^{+4} is to be expected less often than for Th^{+4}.

As regards the bearing of these considerations on the carrying problem, the following statements can be made. Ce^{+4} and U^{+4} compounds are able to carry any proportion of Pu^{+4} in solid solution. Thorium, hafnium and zirconium probably are able to carry limited amounts of Pu^{+4} in solid solution, thorium compounds a higher proportion than hafnium and zirconium compounds.

Trivalent Compounds.-- Crystal chemical similarity to Pu^{+3} is observed for U^{+3}, La^{+3} - Sm^{+3}, Y^{+3}, Bi^{+3}. In Table IV-4 a cross designates that isomorphism is observed, a dash that the known form of the compound is not isomorphous with the known form of the analogous Pu^{+3} compound.

It is believed that the list given above of ions crystal chemically related to Pu^{+3} is complete except for extension to rare earth ions following Sm^{+3} and to such unknown ions as Np^{+3}, Pa^{+3}, Ac^{+3}.

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Table IV-4. Isomorphism for Trivalent Compounds

Compound	U	La	Ce	Pr	Nd	Sm	Y	Bi
PuF_3	x	x	x	x	x	x	-	-
PuOF		x						
$PuCl_3$	x	x	x	x	x		-	-
$PuBr_3$	-	-	-	-	x	x	-	-
PuI_3	x	x						
$PuCl_3 \cdot 6\ H_2O$					x			
PuOCl		x		x	x		x	x
PuOBr		x		x	x			x
PuOI		x						x
$PuPO_4 \cdot 0\text{-}0.5\ H_2O$		x	x		x		x	x

The lack of isomorphism between $PuBr_3$ and tribromides of U, La-Pr is due to the fact that the stability limit of the $PuBr_3$ structure falls between Pu and U and between Nd and Pr.

Values for the ionic radii relative to that of Pu^{+3} as deduced from the crystal structure data are shown in Table IV-5. It is of considerable

Table IV-5. Radii of Trivalent Ions Relative to that of Pu^{+3}

Ion	$R_x - R_{Pu}$	
	F, O	Cl, Br, I
U^{+3}	+.03	+.03
La^{+3}	+.03	+.05
Ce^{+3}	+.01	+.03
Pr^{+3}	-.01	+.01
Nd^{+3}	-.02	0
Bi^{+3}	+.02	
Y^{+3}	-.10	

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interest to note that the values deduced from oxygen and fluorine compounds are not quite the same as those deduced from chlorides, bromides, iodides. This fact is to be ascribed to the greater polarizing influence of the ions with the greater electron density.

The absolute radii for use in oxygen and fluorine compounds are given in Table IV-6.

Table IV-6. Radii for Trivalent Ions

X	R
U	1.06 A
Np	(1.05)
Pu	1.03
La	1.06
Ce	1.04
Pr	1.02
Nd	1.01
Sm	0.99
Eu	(0.97)
Gd	(0.95)
Tb	(0.94)
Dy	(0.91)
Y	0.93
Bi	1.05

The ions U^{+3} and La^{+3}-Sm^{+3} are all excellent stand-ins for Pu^{+3}. The rare earth ions following Sm^{+3} are not as satisfactory stand-ins owing to the decreasing ionic size with increasing number of 4f electrons. Also, Y^{+3} is unsatisfactory as a stand-in. According to ionic size, one would expect a close similarity in crystal chemical behavior between Pu^{+3} and Bi^{+3}. However, in compounds of trivalent bismuth, the chemical binding approaches the covalent type. As a consequence, one may expect to find many instances where trivalent compounds of bismuth and of plutonium are not isomorphous.

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Compounds of U^{+3} and of La^{+3} - Sm^{+3} will certainly be able to carry Pu^{+3} in solid solution in any proportion. Compounds of Y^{+3} and of rare earth ions following Sm^{+3} may carry Pu^{+3} in small proportions.

Trivalent bismuth compounds may be expected to carry large amounts of Pu^{+3} if they are isomorphous with the pure Pu - compounds, but relatively small amounts if this isomorphism does not exist.

Compounds of Metallic Type.-- The radius of Pu for 12-coordination as obtained from the structure of the high temperature form of metallic Pu is 1.63A. Table IV-7 gives a comparison with radii found for some other metals of similar size also in 12-coordination.

Table IV-7. Metallic Radii

Metal	Radius
Th	1.80A
Pu	1.63
La	1.87
Ce	1.82
Pr	1.82
Nd	1.82
Hf	1.58
Tl	1.71
Pb	1.75
Y	1.81
Zr	1.58

The mean radius for U as obtained from the low temperature form is 1.57A. However, the bond type in this structure is apparently not purely metallic and the same is probably true also of the low temperature form of Pu. In all compounds the plutonium radius is about .03A smaller than that of uranium. If this applies also to the metallic

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radius, the density of plutonium would be about 20.2 if the structure were isomorphous with that of the low temperature form of uranium. Conversely, the density of uranium in a structure isomorphous with cubic Pu would be about 15.7.

The observed interatomic distances in the compounds PuO, PuC, PuN, $PuSi_2$ are

Pu-O	2.474A
Pu-C	2.455
Pu-N	2.447
Pu-Si	2.98

Using Pauling's (L. Pauling, Nature of the Chemical Bond, 1939) values for the tetrahedral covalent radii of O, C, N, Si, the following values are obtained for the Pu radius: 1.81A, 1.69A, 1.75A, 1.81A with a mean of 1.76A, which is considerably higher than the radius 1.63A obtained from the structure of the metal.

The experimental data are, however, so meager that a further discussion must be postponed until additional results have been obtained.

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CHAPTER V

PRODUCTION OF PURE COMPOUNDS OF PLUTONIUM

It seemed evident from the beginning of the purification and metallurgy program that, except for a few of the light elements such as the alkalis and alkaline earths, very little purification could be expected in the reduction and metal remelting steps. Indeed, it was the object of much research to learn how to carry out these steps without further contamination of the plutonium with light elements. Emphasis, therefore, was focused upon the development of suitable methods for converting plutonium as received from the producing plants into a pure plutonium compound suitable for reduction to metal. As indicated in Chapter II, the best methods involve a combination of purification by precipitation and solvent extraction, followed by conversion of the purified compound into a plutonium halide. It is the purpose of this Chapter to give a brief summary of the research which led to the process described in Chapter II and to report significant results which might be used to design improved processes.

In the early work on purification it was found that one rapidly reached an inadequate lower level for impurities on successive precipitations or extractions because of the impurity background introduced from chemical reagents, from the air, and from containers. These same sources of contamination also handicapped the development of special methods for the analysis of plutonium for light element impurities (Chapter XI) in the range of their tolerance limits. Difficulties due to reagents were overcome by procuring as many especially pure chemicals as possible from the regular producers and suppliers; others were purified

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by various outside agencies; and those needed reagents which could not be obtained in sufficient purity elsewhere were purified by special groups in the various Project laboratories. A brief account of this work on pure reagents will be found in the last section of this Chapter.

PRECIPITATION METHODS

Few data exist concerning the purification of plutonium compounds by precipitation methods. This is primarily due to the fact that solvent extraction methods appeared to be more promising by the time the supply of plutonium and the development of analytical techniques made direct studies of plutonium purification feasible.

Uranium and Thorium as Stand-ins.-- A considerable amount of work was done using U(IV) and Th(IV) as stand-ins to determine the separation of light elements obtained by precipitating various compounds whose Pu(IV) analogues were known to be insoluble. The elements B, Be, Fe, K, Li, Mg, Na and P were added in the form of their common soluble ions to thorium nitrate or uranous chloride solution in known amounts (ca. 0.1 to 1 per cent of the heavy metal present), and various precipitation procedures were tried. The degree of light element separation obtained was determined by spectrochemical analyses for these elements in all cases.

A detailed discussion of the results obtained does not seem desirable but a summary of the observations from a qualitative point of view is of interest. The following generalizations seem to be justified: (1) precipitations using H_2O_2, $H_2C_2O_4$, HIO_3 (Th only) or $(NH_4)_2MoO_4$ at low pH are more effective than precipitations using reagents (mostly organic) requiring a pH greater than 3 to 4 for precipitation; (2) reprecipitations soon lead to a relatively constant level of impurities

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probably due to contamination from the reagents and vessels used, and to adsorption of impurities by the precipitates; generally one re-precipitation is of value but a second shows little additional separation of the impurities; and (3) phosphorus and silica are difficult to separate by precipitation methods.

Cerium as Stand-in.-- Some work has been done using Ce(III) as a stand-in for Pu(III) in studying the purification to be expected by precipitation of $Pu_2(C_2O_4)_3 \cdot xH_2O$. Results with this stand-in show that of Li, Be, B, Na, Mg, K, V, Cr, Mn, Fe, Ni, Cu, Sr, Mo, Cd, Ba and Bi added in amounts of 1000 ppm each, only Bi is not satisfactorily removed by the oxalate procedure. The others were reduced essentially to or below the tolerance limits.

Precipitants for Plutonium(IV).-- On the basis of the results obtained with stand-ins, the most effective precipitants for Pu(IV) would appear to be H_2O_2, $H_2C_2O_4$ and $(NH_4)_2MoO_4$. These reagents would be expected to reduce B, Be, Fe, K, Li, Mg and Na from about 10,000 ppm to the order of 1 ppm in two precipitations.

SOLVENT EXTRACTION METHODS

Solvent extraction methods for purification have distinct advantages over precipitation procedures. Among the major advantages are: adaptability to continuous processing schemes; continued removal of impurities at very low concentration levels; and a general separation of all the objectionable elements by a single method. Because of these and other advantages, solvent extractions of plutonium compounds were investigated quite extensively.

It is convenient to consider the solvent extraction of inorganic

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plutonium compounds apart from the extraction of organic complexes of plutonium since the factors involved in the two cases are quite different.

Extraction of Inorganic Compounds of Plutonium

Plutonium can be extracted from an aqueous phase into many organic solvents when present as a nitrate in the (IV) or (VI) oxidation state. The factors involved in these extractions are indicated by the existing data but the available fundamental information is not sufficient for a clear understanding of their relative importance.

Effect of Added Salts on Extraction.-- The extraction of plutonium nitrate in the (IV) or (VI) state is very dependent upon the salt concentration in the aqueous phase as shown in Figures V-1 and V-2. In these cases a 1 M HNO_3 solution of plutonium (tracer concentration) was contacted with an equal volume of organic solvent and the distribution of the plutonium was determined as a function of the salt concentration in the aqueous phase.

It is obvious from Figures V-1 and V-2 that the distributions of Pu(IV) and Pu(VI) in these cases are markedly dependent upon the specific nitrate used as well as upon the concentration. In a qualitative sense the nitrate added serves to provide a neutral nitrate compound of plutonium which is soluble in the organic phase, and in addition it serves to "salt out" this compound by decreasing its solubility in the aqueous phase. In the latter role it is probable that the greater the tendency of a particular salt to coordinate water, the greater will be its salting out effect. Speculative interpretations of the limited data on the effects of nitrates upon the distributions of Pu(IV) and Pu(VI) are tempting but of little value and it is hoped that a fundamental investigation

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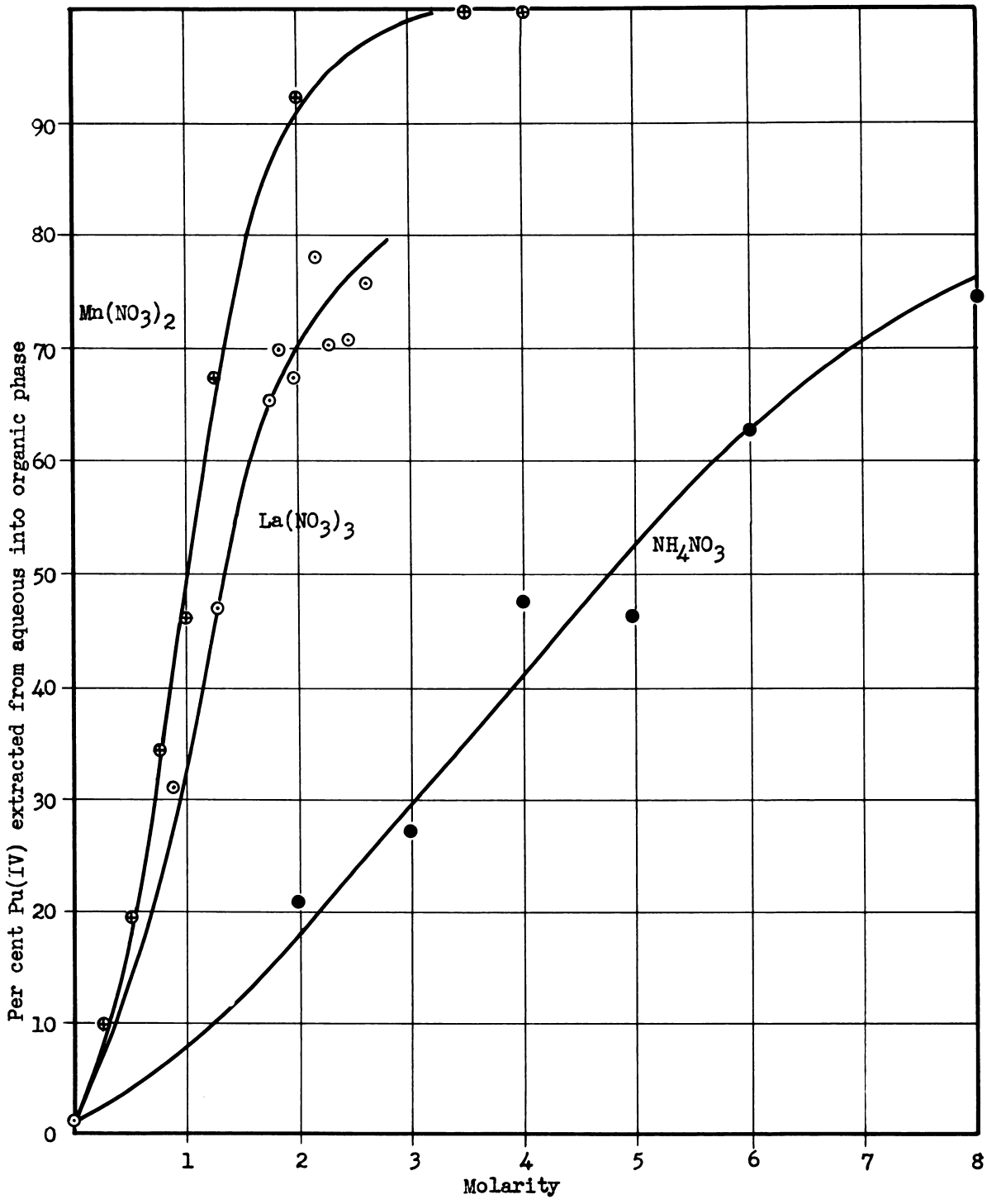

Fig. V-1. Influence of Salts on Distribution of Pu(IV) Between Water and Methyl Isobutyl Ketone (Hexone) at ~25°C.

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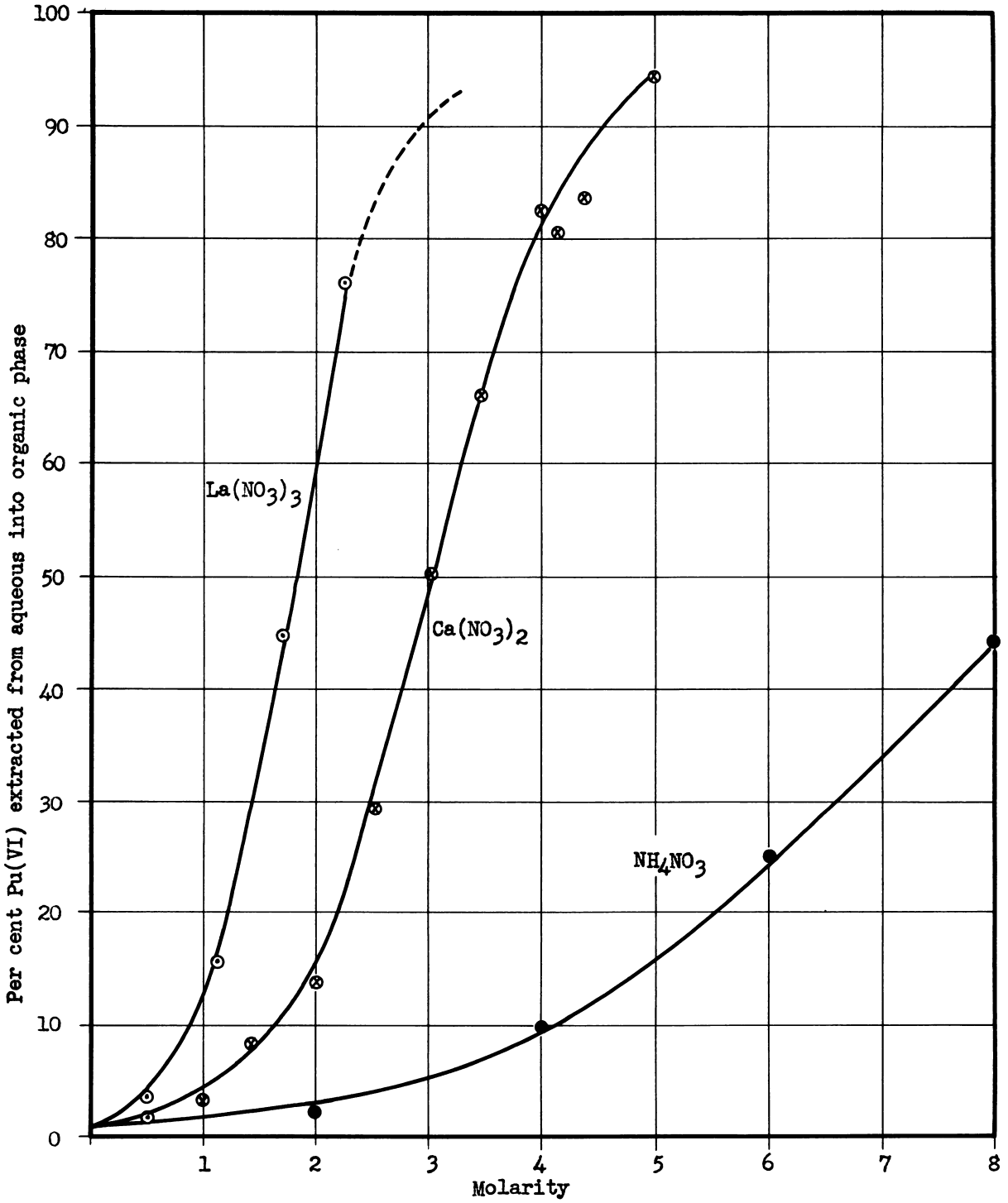

Fig. V-2. Influence of Salts on Distribution of Pu(VI) Between Water and Ether at ~25°C.

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of this problem will eventually be made.

Practically, the relations shown in Figures V-1 and V-2 are useful since it is evident that plutonium can be extracted from an aqueous phase containing a high concentration of a suitable nitrate into an organic phase, and then re-extracted into an aqueous phase containing only enough acid to prevent hydrolysis. In general (as shown in Table V-1), the light elements of interest do not exhibit a similar behavior and may be effectively separated from the plutonium by the use of such a simple extraction cycle.

The general behavior described above is characteristic of the extraction of plutonium as a nitrate by many organic solvents and a large number of such solvents were investigated in the course of the purification program.

Effect of the Solvent.-- The effectiveness of various solvents in extracting plutonium has been compared by determining the plutonium distribution between an arbitrarily selected aqueous phase and an equal volume of each of the solvents to be investigated. An aqueous phase 1 M in HNO_3 and 10 M in NH_4NO_3 was chosen, primarily because it was felt that NH_4NO_3 of high light element purity could be secured. The data obtained are shown in Table V-1. In determining the distribution of Pu(VI), 0.02 M $K_2Cr_2O_7$ was added to the aqueous phase to define the oxidation state of the plutonium. Since many of the solvents listed in Table V-1 are oxidized by acid dichromate solution, the data on the distribution of Pu(VI) are incomplete. In all cases the distributions reported are for tracer scale concentrations of plutonium.

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Table V-1.

Distribution of Plutonium Between 10 M NH_4NO_3, 1 M HNO_3 and an Equal Volume of Various Organic Solvents

Non-Aqueous Phase	Per cent Pu Extracted (IV)	(VI)*
Diethyl ether	35	50
n-Propyl ether	1	4.8 (?)
Di-isopropyl ether	7	1
Allyl ether	3.4	-
n-Butyl ether	1	1.5
Hexyl ether	1	1.5
Ethylallyl ether	2	-
Ethyl-n-butyl ether	1	6
Dichloroethyl ether	3	12
Phenyl cellosolve	21	-
Benzyl cellosolve	48	-
2-Ethylbutyl cellosolve	71	-
Diethyl cellosolve	97	96
Ethylbutyl cellosolve	66	73
β,β'-Dibutoxyethyl ether	93	91 (?)
Dibutyl cellosolve	6	13
Triglycoldichloride	72	-
Dibutoxytetraethylene glycol	73	-
Anisole	3	-
o-Nitroanisole	62	40
p-Fluoranisole	1	-
Resorcinoldimethyl ether	1	-
Dimethyldioxane	60 (?)	-
Dimethyltetrahydrofurane	56 (?)	-
Diethyl sulfide	43	-
Thiophene	1	-
Hexanol	23	-
Heptanol	15	-
2-Ethylhexanol	1	-
Heptadecanol	10	-
2-Ethylbutanol	16	-
Methylisobutyl carbinol	42	-
2-Ethylbutyric acid	5.7	-
Methylethyl ketone + 15% xylene	79	-
Methyl-n-amyl ketone	59	-
Methylisobutyl ketone (hexone)	82	-
Mesityl oxide	14	-

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Table V-1, Continued

Non-Aqueous Phase	Per cent Pu Extracted (IV)	(VI)*
Acetophenone	89	-
Cyclopentanone	91	-
Cyclohexanone	72	-
Methylcyclohexanone	82	-
Menthone	20	47
Isophorone	37	-
Cyclohexane	3	3
Cyclohexene	5	4
Xylene (mixture of isomers)	10	-
Pinene	1.6	-
Indene	5	1
Nitroethane	34	61
Nitromethane	58	61
Nitrobenzene	8	28
Methyl chloroform	4.0	3.2 (?)
Trichloroethylene	6	12
Chlorobenzene	4	7
Bromobenzene	2.6	2.5
Iodobenzene	1.3	1.7
o-Dichlorobenzene	4	5
m-Dichlorobenzene	4.6	-
Ethyl iodide	1	1
Isoamyl chloride	1.6	1
Tertiary amyl chloride	1	-
2-Ethylbutyl acetate	1.5	-
Carbon disulfide	6 (?)	1
Butyl phosphate	99	97

* Dashes refer to cases where the solvent reacted with 1 M HNO_3 containing 0.02 M $K_2Cr_2O_7$ which was present to define Pu(VI).

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Table V-2. Purification by Solvent Extraction

Solvent	Separation Factors for Various Elements x 10^3													
	Al	B	Be	Ca	Fe	K	Li	Na	Mg	P	Bi	La	Ru	Zr
Diethyl Ether	2	~500	0.07	7	0.5	1.0	0.2	1.5	0.5	-	2	L 0.02	L 0.2	L 0.05
Methylisobutyl Ketone	0.1	G0.3	0.2	1.0	0.2	0.1	0.4	2	0.4	L 2	-	-	-	-
Methyl-N-Amyl Ketone	0.2	G 0.3	1.0	2	1.0	0.7	0.6	2	2	4	-	-	-	-
2-Ethylbutyl Cellosolve	0.2	-	1.5	0.3	0.2	-	0.2	0.5	0.2	5	5	0.1	L 0.2	0.1
Triglycoldi-chloride	2	0.25	0.08	G 4	G 4	0.3	0.1	1.0	1.0	L 2	-	-	-	-
Acetophenone	1.3	0.3	0.3	G 3	G 3	-	0.3	0.3	0.7	L 2	-	-	-	-
Menthone	2	-	0.001	G 5	0.1	-	-	-	0.2	-	0.2	L 0.2	L 0.2	L 0.05
Cyclohexanone	0.05	-	1.0	G 5	0.2	2	G 10	6	0.2	-	5	0.2	L 0.2	L 0.05
Ethylbutyl Cellosolve	G 5	-	0.2	0.5	0.5	-	-	-	0.2	-	5	0.05	L 0.2	G 5
Diethyl Cellosolve	1	-	0.3	G 5	0.5	2	G 10	6	0.5	-	5	0.1	L 0.2	0.5
Dimethyltetra-hydrofurane	2	-	1.0	G 5	0.5	-	-	-	0.3	-	5	0.05	L 0.2	0.5
Nitromethane	2	-	0.2	10	L 6	-	30	2	30	0.5	-	-	-	-
Nitroethane	5	-	0.7	40	L 10	-	4	40	10	-	-	-	-	-
Nitrobenzene	0.02	0.3	0.01	3	0.5	-	0.2	4	0.2	L 2	-	-	-	-
Diethyl Sulfide	2	-	3	G 5	2	-	3	4	G 5	-	-	-	-	-
Trichloroethylene	0.1	-	0.1	G 5	0.07	-	6	3	4	-	-	-	-	-

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From Table V-1 it is seen that polyethers, ketones, nitro-compounds and, to a lesser extent, alcohols extract appreciable amounts of plutonium nitrates. The data suggest that extraction occurs by reason of a coordination of the organic solvent with the plutonium through oxygen atoms in the organic compound.

Qualitatively the extent of extraction would be expected to parallel the basicity of the coordinating oxygen atoms. The general trends in degree of extraction shown by closely related organic compounds can be interpreted on this basis. For example, the decrease in per cent extracted in going from diethyl ether to dichlorodiethyl ether, or in going from diethyl cellosolve to triglycoldichloride can be attributed to the decreased basicity of the oxygen atoms due to the action of the chloride atoms which draw electrons away from the ether group in both cases.

The decrease in per cent extraction shown in the type of sequence illustrated by diethyl, ethylbutyl and dibutyl cellosolves suggests that there is a steric factor involved in which the accessibility of the coordinating oxygen atoms influences the degree of extraction.

The type of small decrease in per cent extraction shown by the series hexanol, heptanol and heptadecanol indicates that the dielectric strength of the organic phase is of some limited importance in determining the degree of extraction. Solvents of high dielectric strength would be expected to show a greater degree of extraction if other factors such as basicity and accessibility of the coordinating group were essentially the same.

Application to Purification.-- A direct determination of the separation of light elements from plutonium by the use of the solvents listed

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in Table V-1 was not generally feasible due to the limitations imposed by product availability and the status of the analytical methods. The solvents diethyl ether and methylisobutyl ketone were studied to some extent directly, but a more common method was to determine the separation factors of the light elements using an extraction cycle applicable to plutonium.

The extraction cycle consisted of contacting a 10 M NH_4NO_3, 1 M HNO_3 solution, containing a known amount of the light element studied, with an equal volume of solvent, into which the plutonium would extract. The solvent was then washed with an equal volume of 1 M HNO_3 to remove Pu from the solvent phase, and the fraction of the original amount of a given element which followed plutonium through this cycle was defined as the separation factor for that element. The separation factors observed for a number of the solvents in Table V-1 are shown in Table V-2.

From Table V-2 it can be seen that there is little tendency for the elements listed to be extracted under conditions where Pu(IV) and Pu(VI) can be extracted as nitrates. It would appear that the extractable nitrates are those of small highly charged ions such as U(VI), Pu(VI), Pu(IV), Th(IV), etc., and that extraction drops off rapidly with increased size or decreased charge of the positive ion. For example, extraction is observed to decrease in the order Pu(VI) > Pu(IV) > Th(IV) > Pu(III). On the basis of the data in Table V-2, all of the solvents listed should show good separations of the light elements from plutonium.

Of the solvents discussed above, diethyl ether and methylisobutyl ketone have been studied to a limited extent in the actual purification of plutonium. In the case of diethyl ether, studies of purification of

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U(VI) as a stand-in for Pu(VI) were also made. The results obtained in these cases confirmed the separations which are predicted by the data in Table V-2 and demonstrated the feasibility of using these solvents for the purification of plutonium.

The techniques for carrying out ether or methylisobutyl ketone extractions are of interest. When quantities of the order of a few milligrams of plutonium were purified, batch extractions were generally employed and phase separations of the small volumes involved were obtained by freezing the aqueous layer and decanting the solvent layer. This technique was quite satisfactory. Ether extractions using a Soxhlet type extractor were found to be satisfactory and were used quite extensively for quantities of the order of grams.

At the conclusion of the purification program a continuous countercurrent extraction system had been designed primarily for use with methylisobutyl ketone, although it would be applicable to other solvents. Although this method was not applied to the purification of plutonium, its later tests in connection with the concentration and isolation of plutonium demonstrated better than 99 per cent plutonium recovery and indicated that satisfactory purification could have been achieved.

Studies with Plutonium Chloride and Acetate.-- Various attempts were made to extract Pu(IV) and particularly Pu(III) from solutions containing HCl and NH_4Cl mixtures into each of the classes of solvents listed in Table V-1. In no case was it possible to extract a usable fraction of the plutonium. A few isolated attempts to extract Pu(IV) from acetate solutions into ethylacetate and a few higher alcohols were also unsuccessful. It is quite possible, however, that conditions can be found under

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which the extraction of inorganic compounds of plutonium other than nitrates can be accomplished.

Extraction of Organic Complexes of Plutonium

In addition to the previously mentioned general advantages of solvent extraction methods for plutonium purification, the use of various organic reagents to form extractable plutonium complexes offers the added possible advantage of making the extraction very specific. At the conclusion of the purification program the extractability of a large number of plutonium complexes had been investigated but only a few extractable complexes had been tested to determine their usefulness in purification.

A major portion of the exploratory work on organic complexes of plutonium was carried out on a tracer scale. The organic reagent was added to the organic solvent, except in those cases in which the reagent was water-soluble. The organic solvent was brought into contact with an equal volume of the aqueous phase containing plutonium(IV) tracer, the aqueous phase being buffered to a certain pH with ammonium acetate, and the percentage of the plutonium extracted into the organic solvent was determined. Although some exploratory studies were made with other organic solvents, the bulk of the extractions were made using chloroform. Under these circumstances the observations must be interpreted with some caution for the following reasons: (1) On a tracer scale Pu(III) and Pu(IV) cannot be satisfactorily distinguished. It was generally assumed that in the bulk of the solutions investigated the oxidation state being studied was Pu(IV). (2) The particular solvent or solvents chosen may not have been the most suitable solvents for extraction. (3) Under the

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same conditions which yield good extractions on a tracer scale, the precipitation of plutonium hydroxides might interfere with the extraction when practical concentrations of plutonium are used. (4) The formation of radio-colloids by adsorption of Pu on dispersed phases may yield erroneous results.

Various lines of evidence indicate that the coordination number of Pu(IV) is eight. Therefore, in order to produce a non-polar plutonium complex which might be extractable by organic solvents, the reagent would need to be either a bidentate molecule, containing one acidic and one coordinating group, or a quadridentate molecule, containing two acidic and two coordinating groups. A systematic study was made of the general classes of organic compounds which contain the necessary reactive groups; almost all of the reagents examined were known to form true inner complexes with some elements. Many compounds were selected for the purpose of studying the effect of systematic variations in structure upon complex stability.

Extractions Using Bidentate Organic Reagents.-- The results of most of the work on bidentate compounds are summarized in Table V-3. Very few of these compounds show any promise in the pH range in which no precipitation of plutonium hydroxides would occur. Most compounds were investigated at a variety of pH's in the range 1.0 to 8.0, and in general the percentage of Pu extracted increases with the pH; however, since Pu at practical concentrations would precipitate insoluble compounds at pH's higher than six unless an extremely stable complex was formed, only the percentage extracted at the highest pH under or equal to seven is listed for each compound in the Table.

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Table V-3. Behavior of Tracer Pu(IV) with Various Bidentate Compounds - Chloroform as Solvent

Type of Reagent	Reagent	Carrier	pH	% Pu Extracted
Hydroxy-ketones	Benzoin	-	6.0	1.3
	2-hydroxy-5-methyl benzophenone	-	6.2	0.3
	2-hydroxy-benzophenone	-	6.3	0.5
Diketones	Benzoylacetone	-	5.5	7.0
	Dibenzoylmethane	-	5.7	36.0
Oximes and Nitroso Compounds	α-Nitroso-β-naphthol	Co^{++}	6.0	10.7
	β-Nitroso-α-naphthol	Co^{++}	6.0	7.6
	o-Hydroxyacetophenone oxime	Cu^{++}	6.0	13.0
	α-Benzoin oxime	Cu^{++}	6.0	3.4
	Acetylacetone dioxime	-	6.0	1.0
	Dimethylglyoxime	Ni^{++}	6.0	4.2
	Isonitroso-acetophenone	-	5.8	1.9
	Isatin-β-oxime	Cu^{++}	6.7	2.5
Monoimines	Acetylacetonemonoimide	-	7.0	1.0
	Salicylalmethylimine	Cu^{++}	6.0	0.8
	Salicylalethylimine	Cu^{++}	6.0	0.8
	Salicylal(β-hydroxyethyl)imine	Cu^{++}	6.6	1.0
	Salicylalphenylimine	Cu^{++}	6.0	7.2
	Salicylal (2-hydroxyphenyl)imine	Cu^{++}	6.4	49.2
O-Hydroxy-Azo Compounds	2-Hydroxy-5-methyl azobenzene	Cu^{++}	5.8	1.0
	1-Benzeneazo-2-hydroxynaphthalene	Cu^{++}	7.0	1.0
	p-Nitrobenzene-azoresorcinol	-	6.0	5.4
Hydroxamic Acids	* Benzohydroxamic acid			
	O-Hydroxybenzohydroxamic acid	-	6.0	2.9
	α-Furohydroxamic acid	-	6.7	5.9
Dithiocar-bamates	Ammonium phenyldithiocarbamate	-	7.0	1.0
	Ammonium morpholine dithiocarbamate	-	5.5	0.7
Miscell-aneous Bidentate Compounds	Diphenylthiocarbazone	Ni^{++},Co^{++}	7.0	1.0
	Diphenylthiourea	Cu^{++}	6.0	3.0
	α-Picolinic acid	Co^{++}	7.0	1.0
	Diphenylcarbazide	Cu^{++}	6.9	6.7
	Salicylalphenylhydrazone	-	7.0	1.0
	O-Hydroxyacetophenone-semicarbazide	-	6.0	14.1
	O-Aminophenol	Cu^{++}	6.0	4.3
	Anthranilic acid	Cu^{++}	6.1	1.3
	α-Azobenzene-β-ketobutyric acid	-	5.5	1.0
	Rhodanine	Cu^{++}	6.7	1.0
	N-Methylsalicylamide	-	6.2	1.9
	N,N'-Diphenylformazylbenzene	-	5.9	1.2

* Extractions using benzohydroxamic acid reveal an interesting phenomenon -- at pH = 1.9, 7.6 per cent of Pu(IV) is extracted, there is a rise to a maximum of 21.5 per cent extraction at pH = 3.35, followed by a minimum of 6.8 per cent at pH = 4.5. The per cent extracted then rises with pH, 65.5 per cent being extracted at pH = 7.61.

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When quinalizarin is used as the reagent with aniline as solvent and Zr as carrier, approximately 95 per cent of tracer Pu was extracted with the original aqueous phase buffered at a pH in the range 2.1 to 5.5. These results are not very significant, however, because aniline without a complexing reagent will extract approximately 85 per cent of tracer plutonium; furthermore, the pH of the aqueous phase was increased due to the solubility of aniline in water. It also is significant that with quinalizarin as complexing reagent, no appreciable amount of Pu is extracted into such solvents as diethyl ether, t-amyl alcohol, nitromethane and petroleum ether.

With salicylaldoxime as complexing reagent and solvents such as nitromethane and aniline, extractions as high as 72 per cent were obtained in some of the early exploratory work in the pH range from 4 to 6. With chloroform as solvent, results were difficult to duplicate. Since extractions were greatest when hydroxylamine or large amounts of Co^{++} carrier were present, it might be inferred that reduction to Pu(III) is necessary to obtain complexing with salicylaldoxime.

Extractions Using Quadridentate Organic Reagents.-- Preliminary investigations with quadridentate compounds showed that less than 2 per cent of tracer Pu(IV) was extracted into chloroform in the practical pH range (< 7.0) when o-hydroxyacetophenone ethylenediimine and bisacetoacetonyl ethylenediimine were used as complexing reagents; however, complexing with disalicylaldiimines showed considerable promise. The latter are Schiff's bases prepared by condensing diamines with o-hydroxy aldehydes or ketones, one of the simplest examples of this

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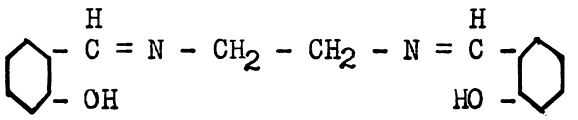
type of reagent being disalicylalethylenediimine



A systematic investigation of these Schiff's bases was undertaken, first to determine the length of the hydrocarbon chain between the two imino groups which would favor most complete complexing of Pu(IV). From the results of these experiments listed in Table V-4, it is evident that the optimum length of hydrocarbon chain is that containing two carbon atoms. It having been determined that the ethylenediimine was the most effective disalicylaldiimine, twenty-one derivatives of this diimine were studied to determine the effect of substituted groups on their behavior as complexing reagents. These results are summarized in Table V-5. It will be noted that a number of these derivatives are fairly effective over a wide range of pH, including pH's well below that at which plutonium hydroxides precipitate.

One exceptionally promising derivative, di(2,3-dihydroxy-5 or 6-tertiary-butylbenzal)-ethylenediimine, has been investigated in the extraction of Pu(IV) on the microscale by the following procedure: The Pu(IV) (H_2O_2 reduced) was contained in about 2 ml. of solution buffered with acetate to a pH of approximately 4.0. A five-fold excess of the solid organic reagent was added and the slurry agitated with a quartz rod. The formation of the Pu complex was accompanied by a change in color from yellow to chocolate brown. Two ml. of chloroform were added and the extraction carried out in a manner similar to that used for cupferron extraction (Chapter XI). Although a long time (35 to 50 hrs.) was required to obtain fairly complete extraction at temperatures of 25° to 30°C., extraction was quite complete in one hour at 95°C.

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Table V-4.

Extraction of Tracer Pu(IV) by Various Disalicylaldiimines and Chloroform

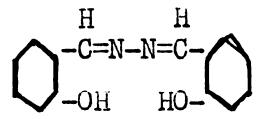
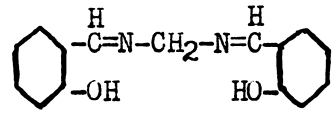
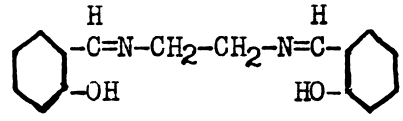
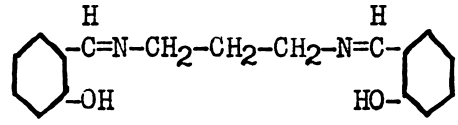
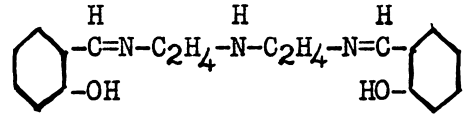
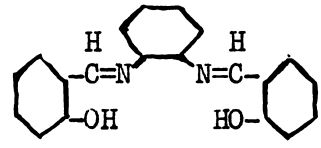
Compound		pH	Per cent Extracted
Disalicylalhydrazine		2 4 6 8	0 4.1 9.4 0.6
Disalicylamonomethylenediimine		2 4 6 8	2.5 0.6 3.1 0.9
Disalicylalethylenediimine		4.59 5.00 5.52 5.74 6.00	20.5 76.6 93.0 98.6 97.3
Disalicylaltrimethylene-diimine		3.32 4.38 4.90 5.40	0.5 25.0 12.5 1.3
Di-(2-hydroxybenzal-iminoethyl)-amine		2 4 6 8	0.6 0.5 23.8 25.2
Disalicylal-o-phenylene-diimine		2 4 6 8	0.2 22.5 14.0 3.5

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Table V-5.

Extraction of Tracer Pu(IV) by Chloroform
and Various Derivatives of Disalicylalethylenediimine

Reagent	pH	Per cent Extracted
Di-(2-hydroxy-5-methylbenzal)-ethylenediimine	3.20	11.8
	4.82	31.3
	5.68	87.0
	6.09	97.4
Di-(2,3-dihydroxy-6-phenylbenzal)-ethylenediimine	2.85	43.8
	4.00	56.8
	5.12	69.1
	5.98	86.0
Di-(2-hydroxy-3-bromobenzal)-ethylenediimine	2.61	28.8
	3.20	49.5
	3.88	26.0
	5.05	20.2
	5.80	39.7
	6.30	75.5
Di-(2-hydroxy-3-chlorobenzal)-ethylenediimine	2.88	82.0
	3.36	69.5
	4.42	57.2
	5.45	75.6
	6.00	71.4
Di-(2-hydroxy-5-chlorobenzal)-ethylenediimine	2.33	26.2
	3.30	85.5
	4.20	50.8
	5.02	47.0
	6.15	82.0
Di-(2-hydroxy-3,5-dichlorobenzal)-ethylenediimine	2.48	54.4
	3.26	83.9
	4.55	53.8
	5.00	62.0
	5.85	71.0
Di-(2-hydroxy-3-chloro-5-tertiary-butylbenzal)-ethylenediimine	2.08	59.0
	2.75	97.1
	3.62	99.5
	4.12	99.4
	5.66	94.0
Di-(2-hydroxy-3-bromo-5-tertiary-butylbenzal)-ethylenediimine	1.98	0.8
	3.22	40.4
	3.59	71.0
	4.53	43.0
	5.50	65.0
	5.98	92.0

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Table V-5, Continued

Reagent	pH	Per cent Extracted
Di-(2-hydroxy-3-isopropyl-5-chloro-6-methylbenzal)-ethylenediimine	3.61	46
	4.70	81
	5.82	89
Di-(2-hydroxy-3,5-dimethylbenzal)-ethylenediimine	2.72	50.7
	3.90	61.8
	5.00	61.7
	5.98	85.6
Di-(2-hydroxy-3-chloro-4-tertiary-butylbenzal)-ethylenediimine	2.23	58.2
	2.91	83.3
	3.85	71.8
	4.59	52.4
	5.16	75.6
	5.75	92.9
Di-(2-hydroxy-5-tertiary-butylbenzal)-ethylenediimine	2.89	41
	4.52	89
	5.16	91.4
	6.08	84.7
	6.98	21.0
* Di-(2,3-dihydroxy-5 or 6-tertiary-butylbenzal)-ethylenediimine	1.55	3
	1.98	83.5
	2.75	97.2
	2.95	99.9
	3.98	99.6
	4.42	99.7
	4.92	98.0
	5.30	98.8
	5.60	99.2
	6.40	91.0
Di-(2-hydroxy-5-tertiary-amylbenzal)-ethylenediimine	2.62	6.9
	3.52	54.2
	4.62	69.3
	5.28	80.0
	6.14	77.6
Di-(2-hydroxy-4,6-dimethylbenzal)-ethylenediimine	1.20	0.9
	4.08	4.5
	4.91	31.4
	5.47	85.7
	6.22	84.7

* The position of the tertiary-butyl group is not definitely known. The parent aldehyde was prepared by the Duff reaction from 2-hydroxy-4-tertiary-butylphenol, and the tertiary-butyl group might be in either the 5- or 6-position. Exhaustive attempts to prove the structure of the parent aldehyde by several series of reliable reactions have failed to elucidate the position of the tertiary-butyl group.

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In addition to the derivatives listed in Table V-5, the following were tried but yielded less than 60 per cent extraction at any pH in the range 2 to 7:

Di-(2-hydroxy-3-methoxybenzal)-ethylenediimine;

Di-(2-hydroxy-3-nitrobenzal)-ethylenediimine;

Di-(2-hydroxy-5-chloro-6-methylbenzal)-ethylenediimine;

Di-(2-hydroxy-3-methyl-5-tertiary-butylbenzal)-ethylenediimine;

Di-(2-hydroxy-diamylbenzal)-ethylenediimine; and

Di-(2-hydroxy-(6-methyl-5-tertiary-butyl-and/or 4-methyl-5-tertiary-butyl)-benzal)-ethylenediimine.

Applications to Purification.-- The low percentages of Pu(IV) extracted into chloroform from aqueous solutions at pH's < 1.6 when di-(2,3-dihydroxy-5 or 6-tertiary-butylbenzal)-ethylenediimine was used as a complexing reagent indicated that the complex would be destroyed by acid, permitting the transfer of plutonium from the chloroform solution of the complex back into an aqueous phase. Indeed, this cycle can be used effectively as is demonstrated by the data in Table V-6 which were obtained using the procedure for extractions outlined above, the re-extractions being accomplished with a volume of aqueous acid solution equal to the volume of the chloroform solution.

It should be noted (Table V-6) that plutonium is almost completely re-extracted from the chloroform solution of the complex by 0.2 N HNO_3, whereas the copper complex is stable at this acidity and remains in the chloroform. This suggests that even though the complexing reagent is not as specific for plutonium as might be desired, a significant purification may be accomplished by the judicious selection of the pH's

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Table V-6

Stability of Tracer Pu(IV) Complex of
Di-(2,3-dihydroxy-5 or 6-tertiary-butylbenzal)-ethylenediimine
Toward Dilute Acid (Cu^{++} Carrier)

pH of initial extraction	% of Pu extracted into $CHCl_3$	Normality of HNO_3 used to destroy complex	% of Pu extracted from $CHCl_3$ into acid	% Yield of Pu thru both cycles	Remarks
3.91	99.7	1.0	99.5	99.2	Reagent attacked by acid.
3.92	99.0	0.4	99.6	98.6	Cu^{++} complex destroyed; reagent somewhat attacked.
3.98	98.7	0.2	99.2	97.9	Cu^{++} complex stable
3.93	98.7	0.05	83.7	82.6	"

at which the extractions into chloroform and the re-extractions into aqueous acid solutions are made. Further experiments with di-(2,3-dihydroxy-5 or 6-tertiary-butylbenzal)-ethylenediimine as complexing reagent have revealed the following facts pertinent to plutonium purification:

(1) This complexing reagent does not react with trivalent elements; the rare earths are not extracted under conditions which lead to essentially complete extraction of Pu(IV). Very satisfactory separations from lanthanum have been demonstrated even when Pu(IV) is present in only tracer amounts and La^{+++} is present to the extent of 5.0 mg. per ml.

(2) Complexes are formed with Ba^{++} and Mg^{++} but extraction of these is low in the pH range in which essentially complete extraction of Pu(IV) is obtained.

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(3) Many of the complexes formed by this reagent with other tetravalent ions are less stable toward dilute acid than are its complexes with Pu(IV).

(4) The alkali metal ion, Cs^+, is not extracted into chloroform under conditions which permit complete extraction of the Pu(IV) complex.

PREPARATION OF PURE PLUTONIUM HALIDES

Only two halides, the tetrafluoride and the trichloride, have been extensively studied and seriously considered for use in the routine production of highly pure plutonium metal.

The guiding principle has been that the halide should be prepared from a compound appropriately purified by precipitation and solvent extraction methods in such a fashion that no harmful contaminants are introduced in the "dry" treatments. In other words, the halide would be expected to be as pure as, but not purer than, the "wet" purified material going into the halide manufacture. Since neither hydrogen fluoride nor hydrogen chloride are likely to introduce light element impurities (other than the halide itself), and since materials are available for use as containers and reactors which also do not add significant impurities to the halide, it has appeared that either the tetrafluoride or trichloride (or, for that matter, trifluoride and tribromide) can be manufactured with equal purity.

Plutonium Tetrafluoride.-- The tetrafluoride is made from a purified Pu(III) oxalate slurry as follows. The slurry is handled in a Pyrex container (quartz would have been used if the need for extreme high purity

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had continued), and is transferred through a Pyrex tube into a weighed platinum tray contained in a vacuum drying chamber. The slurry is quickly dried under a slight vacuum at about 50°C. to $Pu_2(C_2O_4)_3 \cdot xH_2O$ (x is usually close to 9). According to the present technique the tray is then placed in a muffle furnace and the oxalate ignited, gently at first, then to 1000°C., producing a dense mass of PuO_2. This is weighed to give an accurate measure of the amount of Pu present, then the tray is placed in a large nickel tube reactor and treated with a fast stream of tank HF plus O_2 (mol-ratio HF:O_2 about 8:1) at a temperature of 800°C. Runs on the 1 to 7 gram scale have required about 6 hours of hydrofluorination. The pink PuF_4 formed is then weighed to check the completeness of conversion, which is generally 99.7 per cent or better. Since the compound is not very hydroscopic it needs no special handling except for health precautions. The tetrafluoride may be made more quickly by direct hydrofluorination of the oxalate, but the product is somewhat fluffier and the denser variety made from oxide is preferred for reduction by the metallurgists.

Plutonium Trichloride.-- The trichloride is made in a similar fashion from the Pu(III) oxalate, except that ignition to PuO_2 is avoided because the latter hydrochlorinates very slowly. Instead, the oxalate is dehydrated in a quartz tube reactor by passing oxygen-free H_2 over the $Pu_2(C_2O_4)_3 \cdot xH_2O$ at about 150°C. Then, without cooling, anhydrous hydrogen chloride, purified by fractional distillation, is admitted in a very fast stream (mol-ratio HCl:H_2 about 2:1) and the oxalate is heated at about 250°C. for several hours. Finally, it is taken up to about 650°C. and held there several hours, then cooled in the gas stream to room temperature. Weighing

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in a closed container serves to check the conversion which is generally 99.5 per cent or greater. The trichloride should be kept out of contact with moist air.

Metal made from the trichloride has come surprisingly close to meeting the tolerance limits for light element impurities (see Chapter II).

Plutonium Trifluoride.-- Samples of PuF_3 made from $Pu(NO_3)_4$ by the following series of reactions have been analyzed for the light elements Al, Be, Ca, Li, Mg and Na. The $Pu(NO_3)_4$ had been purified by ether extraction.

$$2Pu(NO_3)_4 + 2H_2O + SO_2 = 2Pu(NO_3)_3 + H_2SO_4 + 2HNO_3$$

$$Pu(NO_3)_3 + 3HF\ (aq) = PuF_3\ (s) + 3HCl$$

$$PuF_3\ (s)\ (300^{\circ}C.\text{in stream of HF gas}) = PuF_3\ (\text{anhydrous}).$$

From the analytical results (Table V-7) it is evident that the PuF_3 thus produced was of a purity equal to or greater than that of the blanks.

Table V-7. Analyses of PuF_3 (ppm)

Element	Blank I	Blank II	Sample I	Sample II
Al	10	10	L 10	L 10
Be	L 0.2	L 0.2	L 0.2	L 0.2
Ca	300	300	200	100
Li	30	30	1	0.5
Mg	40	40	20	10
Na	200	200	100	50

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PREPARATION OF PURE REAGENTS

In all attempts to prepare pure plutonium compounds by any method or to study purification procedures using stand-ins considerable difficulty was experienced in avoiding contamination in the processing. Contamination from the vessels used, the reagents employed and from the air was found to be serious.

The latter source was eliminated fairly successfully by the use of "Precipitron" cleaned air in laboratories which were kept as clean as possible by daily washing, and by carrying out operations in enclosed systems wherever possible.

A study of the light element contamination of HNO_3, HCl, H_2SO_4 and NH_4OH solutions by contact with Pt, quartz and Pyrex vessels, was initiated but not completed. The results in HNO_3 and HCl solutions indicated that quartz or Pt were probably satisfactory but Pyrex in general was not.

This same problem of contamination was also encountered in the development of special methods for the analysis of plutonium and its compounds for light element impurities (Chapter XI). In addition to providing cleaned air and suitable containers, considerable effort has been expended on the procurement and preparation of pure reagents.

Pure Gases

Commercial gases as obtained in tanks are relatively impure, containing from < 0.5 to 5 per cent impurities, depending on the source and the method of purification (if any) used by the manufacturer. The gases of particular use in the purification of plutonium and the preparation of pure plutonium compounds are oxygen, hydrogen, nitrogen, helium, argon, hydrogen

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chloride, hydrogen bromide, bromine, chlorine, hydrogen fluoride and fluorine.

Oxygen.-- most oxygen obtained commercially is made by the rectification of liquid air. The principal impurity is nitrogen, plus a small amount of argon, although it also contains small amounts of water and possibly some oil from the compressors. Small amounts of CO_2 and CO might also be present from the oxidation of carbonaceous materials in the tank and compressors. Everything except the argon and N_2 can be removed by passing the O_2 over hot CuO ($\sim$700°C.), (or hot platinized asbestos) and through a drying tower of $Mg(ClO_4)_2$ or P_2O_5. For most purposes the nitrogen impurity is of no consequence and will not interfere because nitrides are readily converted to oxides at elevated temperatures in oxygen.

However, if oxygen free from nitrogen is needed it can be prepared from $KClO_3$ using MnO_2 as a catalyst. A small amount of Cl_2 is formed as an impurity in this process but this can be removed by bubbling the O_2 through a solution of NaOH and then through a drying tower. An Ascarite tower followed by a drying tower can also be used to remove Cl_2 from O_2 made in this manner. Electrolytic oxygen is very pure, being contaminated only with a small amount of H_2 and water vapor. These can be removed by catalytic oxidation of the hydrogen and removal of the water with a drying tower.

Hydrogen and Deuterium.-- Hydrogen as purchased commercially is contaminated with oxygen, water vapor and some oil from the compressors. The classical methods of purification are: (1) to pass the H_2 over hot Cu and then through a drying tower; or (2) to pass the H_2 over hot platinized asbestos and then through a drying tower. The efficiency of these methods is open to some question since the hydrogen so obtained will still attack

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a polished U surface at 600°C., at which temperature no hydride should form. The use of a liquid air trap following the drying trap should improve the efficiency of the purification.

Pure H_2, free from all contamination, including the rare gases, can be made by decomposing uranium hydride, from which all gases have been evacuated while at room temperature, by heating the hydride to 430°C., at which temperature the decomposition pressure of UH_3 is near one atmosphere. The container is then flushed a few times by allowing the gas to escape into an evacuated system. The hydrogen evolved following this initial flush of H_2 is very pure. The best arrangement is to have about 1 mole of U in a 500 ml. Pyrex bulb which can be heated externally by a resistance furnace. The bulb is connected to the system through a sintered glass disc and a stopcock. The sintered disc is important to prevent the blowing of hydride through the system when the hydrogen is admitted to an evacuated space.

The above process is a batch process and for larger quantities of hydrogen a continuous process can be used by passing the hydrogen over uranium turnings or powdered uranium metal (decomposed hydride) in a quartz or Corning #172 glass tube which is heated to 700° or 800°C. by a resistance furnace. For rates up to 1 liter per minute a unit 6 in. long is sufficient to purify the H_2 so that it does not attack U at 600°C. If faster flow rates are desired the unit will have to be made correspondingly longer. It has been shown that H_2 purified in essentially this manner reacts with U metal at 200° to 300°C. with a shorter incubation period than when purified by ordinary methods.

Nitrogen.-- The two classical methods of purifying N_2 to free it from O_2 (the principal impurity) are: (1) to pass it through alkaline

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pyrogallol solution, followed by a drying tower; or (2) to mix it with an excess of H_2 (over the O_2 present), pass it over hot platinized asbestos, then over CuO to remove the excess H_2, and finally through a drying agent.

Nitrogen essentially free from all impurities except the rare gases and oxygen can be prepared by oxidizing the hydrocarbons, CO, and H_2 to CO_2 and water by hot CuO (~600°C.), removing the resulting CO_2 and H_2O with towers of Ascarite and $Mg(ClO_4)_2$, respectively. The oxygen is then removed in a final step by passing the mixture over hot uranium nitride, the uranium nitride (composition $UN_{1.5}$ to $UN_{1.75}$) being oxidized to UO_2 and nitrogen liberated from the nitride by the reaction:

$$UN_{1.75} + O_2 = UO_2 + 0.375\ N_2$$

This process has been shown to be nearly 100 per cent efficient for removing O_2 from N_2 when the nitride is at a temperature between 300° and 600°C. Higher temperatures are probably not harmful but are unnecessary.

The condition of the nitride in such an apparatus is of great importance. The usual nitride obtained by reaction of N_2 or NH_3 on UH_3 is a very fine powder and is very difficult to pack into a column in such a manner that gas can flow through it readily. Usually it blows out of the system even with glass wool plugs in the ends of the tower. A more granular nitride, much more suitable for use in the nitride tower, can be made by passing N_2 or ammonia over uranium turnings at 800° to 900°C., being careful (if NH_3 is used) to form no hydride. This material usually has the shape of the original turnings (though sometimes it is a powder) and although the granules are rather brittle and easily pulverized they can be packed into the tower with suitable glass wool spacers (1/8 to 1/4 in. thick alternate layers of nitride and glass wool) so that at 5 psi pressure

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of N_2 on the inlet side of the system, up to 5 liters per minute of N_2 can be passed through the purifier.

Tests with an alkaline solution of pyrocatechol and ferrous sulfate show that with towers 12 in. high, no O_2 is present in the N_2 from the exit at rates of gas flow up to 1 liter per minute, the fastest rate tested. A single packing of a tower of this size will purify a full 200 cu. ft. tank of water pumped commercial nitrogen.

Noble Gases.-- The noble gases of principal interest to the Project as inert atmospheres for handling various materials are helium and argom; these being the cheapest and most readily available of the inert gases. The method outlined here depends only on their lack of chemical activity so it can be used for all of the inert gases in Group VIII of the Periodic Table. If small amounts of the rarer gases, Ne, Kr or Xe, are to be purified, provision must be made in the apparatus for handling and collecting the small amounts of gas used; otherwise, the method will be the same as that outlined below.

The best material for purifying the rare gases is powdered, partially sintered uranium metal made by decomposing UH_3 at 300° to 400°C. under vacuum. At 750° to 800°C. uranium turnings react with all gases, except H_2 and rare gases, to form stable compounds (e.g., CO and CO_2 to form UC and UO_2, respectively, CH_4 forms UC + H_2, H_2O forms UO_2 + H_2, etc.). Thus, after passing the rare gases over powdered metal at 750° to 800°C., the only remaining components are the rare gases and H_2. The H_2 can be removed (1) by passing the gas over hot CuO followed by a drying tower, or (2) by passing it over a cold section of powdered metal, where even at room temperature the hydrogen will react to form UH_3.

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Since the decomposition pressure of UH_3 at room temperature is only about 10^{-5} mm., the amount of H_2 remaining in the gas stream after procedure (2) is negligible. In procedure (1) there is danger of contaminating the rare gases with oxygen since CuO has an appreciable vapor pressure of O_2 at 500° to 600°C.

A convenient method of purifying the rare gases is to fill a 24 to 30 in. tube of silica or Corning #172 glass, preferably silica since the temperature is high for #172 glass, with powdered metal using a glass wool plug in each end to keep the metal in place, heat a 4 to 6 in. section at the gas entrance end of the tube to 750° to 800°C. and allow a temperature gradient down the tube, the exit end being at room temperature. Rare gases purified in this manner will not attack a polished uranium surface at temperatures up to 600°C. Above 660°C. the test fails since the surface naturally loses its polished character due to the recrystallization of the metal in passing to the β form and back again on cooling.

Hydrogen Chloride.-- Hydrogen chloride can be purified from water, chlorine and oxygen by passing it through a P_2O_5 tower and then over UCl_3 at 400°C. This will remove water and oxygen to a lower limit such that they will not interfere in the preparation of the halides of product or uranium. Tank HCl when purified in this manner will form no detectable oxy-chlorides in UCl_3 prepared by the action of HCl on UH_3.

Chlorine.-- Tank chlorine can be purified from O_2 and H_2 by passing it over UCl_4 at 400°C., the UCl_4 being oxidized to UO_2Cl_2 by any oxygen present (some may go completely to UO_2 or U_3O_8). The UCl_4 may be prepared by the action of Cl_2 on UCl_3. Some higher chlorides are formed

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in the UCl_4 by action of Cl_2 at this temperature and these distill to cooler portions of the tube. The dust may be removed from the gas stream by glass wool or sintered glass filters in a cold portion of the apparatus.

Hydrogen Bromide.-- HBr must be prepared as needed. The most convenient methods of preparation are:

(a) The reaction between tetralin (tetrahydronaphthalen) and Br_2. The tetralin must be dehydrated first and pure Br_2 added. Bromine can be almost completely removed by bubbling the HBr through a scrubber containing tetralin. In this method only one-half the bromine is converted to HBr, the rest being used to brominate the tetralin.

(b) The catalytic reaction of H_2 and Br_2 on platinized asbestos or pieces of clay plate. This usually contains some excess H_2 which is usually not a harmful impurity for most uses and it may contain a little unreacted Br_2. The H_2 must, of course, be purified if pure HBr is to be obtained.

The HBr as obtained by either of these methods may be purified by passing it through a P_2O_5 tower followed by UBr_3 at 400°C. The UBr_3 can be prepared by action of HBr on UH_3 at 300°C. This effectively removes all Br_2, O_2 and H_2O from the HBr stream.

Bromine.-- Bromine is usually carried by an inert gas stream. The inert gas should be purified (N_2, A or He may be used for most purposes). Reagent grade, redistilled bromine as purchased contains carbonaceous materials and water and should be redistilled from P_2O_5 before use.

A bromine vapor - inert gas mixture - may be purified by passing it over hot UBr_4 at 400°C. Any O_2 or water is removed to form UO_2Br_2, $UOBr_2$ or UO_2.

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Hydrogen Fluoride.— Anhydrous HF as obtained commercially contains 0.5 to 1 per cent water. This water may not be a harmful impurity for most uses, but if it is necessary to have greater purity than this one can pass the HF over UCl_5 or UF_5, or the mixture. Uranium pentafluoride for this purpose may be prepared by the action of HF on UCl_5 at 300°C. or by partially fluorinating UF_4. In case UCl_5 is used, the gaseous HF could be condensed on the UCl_5 and liberated as needed. Small quantities of HCl are liberated by hydrolysis in the removal of the water, and if this is a harmful impurity, UF_5 must be used. Alumina has also been used for drying anhydrous HF.

It has been found that HF drawn from cylinders contains appreciable amounts of H_2. Presumably, H_2 is produced by the action of HF on the cylinder wall and accumulates in the gas phase. Oftentimes the amount of H_2 is sufficient to bring about the formation of PuF_3 when the preparation of PuF_4 is intended. Hydrogen fluoride essentially free from H_2 may be obtained by bleeding the gas phase containing H_2 from the cylinder before HF is withdrawn for use, or by inverting the cylinder and withdrawing HF from the liquid phase.

Fluorine.— Fluorine will contain HF and CF_4 as impurities, with possibly some O_2 and N_2 if care is not taken to sweep out the electrolytic cell well before use. The amount of HF will depend on the composition of the bath and the temperature of the bath, while the amount of CF_4 will depend on the composition of the anode and the amount of carbonaceous material in the anode and bath.

The HF and CF_4 may be removed by passing the F_2 through the following successive traps: (a) Trap at -80°C. of dry-ice and trichloroethylene.

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This removes most of the HF. (b) Trap containing anhydrous KF. This removes the remaining HF to form the double salt KF·HF. (c) Trap at liquid oxygen temperatures which removes the CF_4.

Pure Liquid and Solid Reagents

The liquid and solid reagents which were procured or prepared in a state of special purity are listed in Table V-8. These reagents include both analytical reagents of extreme purity and processing reagents. The specifications were based upon the final product tolerance limits and were then modified in the case of each reagent in accordance with the tendency of the particular element to interfere with the specific use of the reagent. The Table contains the analyses obtained on the best reagent produced in each case, thus indicating the purity which it has been possible to obtain.

In general, purification of acids was by distillation or solution of the anhydrous acid in water. Most of the salts were purified by crystallization of the salt itself or of an intermediate from which it was prepared. The barium metal is a sample of a commercially distilled material.

A reagent of interest which was prepared for use in the determination of aluminum by fluorescence was maclurin. In an attempt to prepare a satisfactory crystalline morin, it was discovered that the maclurin fraction of crude morin is much more effective for the preparation than the pure morin fraction.

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Table V-8. Analyses of Purified Reagents

Element	Al	Be	Ca	Fe	K	Li	Mg	Na	Si	B	F	Cl
Final Product Tolerance	11 ppm	0.06	2×10^{3}	2×10^{3}	1×10^{3}	1.2	6	5.2	50	0.2	1.5	200
Reagent												
Ammonium hydroxide	2×10^{-3}	5×10^{-6}	0.2	10^{-2}	0.5	5×10^{-5}	10^{-2}	0.4	0.5	-	-	-
Ammonium molybdate(1)	L0.2	L2×10^{-3}	L0.3	L0.5	L0.3	L2×10^{-3}	L0.1	0.5	L0.1	0.15	L5	L5
Ammonium nitrate	1	2×10^{-2}	L5	L1	-	L0.05	L2.0	3	L1	-	-	0.4
Barium bromide, anhyd.	50	L0.2	5	L50	10	L1	5	10	-	-	-	10^{3}
Barium iodide, anhyd.	No analysis											
Barium metal(2)	L6	L3×10^{-2}	30	L55	-	L0.3	L11	55	L6	0.5	225	20
Bromine	No analysis											
Calcium metal	L9.0	L5×10^{-5}	-	L90	200	5×10^{-5}	L18	20	L45	0.6	L5	2800
Hydrochloric acid(2)	8×10^{-4}	8×10^{-5}	2×10^{-2}	0.2	-	2×10^{-5}	8×10^{-4}	2×10^{-2}	4×10^{-3}	10^{-2}	-	-
Hydrogen peroxide	2×10^{-3}	5×10^{-6}	7×10^{-3}	2×10^{-2}	-	L5×10^{-5}	L2×10^{-3}	5×10^{-2}	3×10^{-2}	10^{-3}	10^{-2}	-
Iodine(1),(2)	L5.0	-	-	L5	-	L10^{-2}	L5	L5	-	0.1	0.5	L7.5
M-Nitrobenzoic acid	L5	L2.5×10^{-2}	2.5	L5	-	5×10^{-2}	L1	L10	1	L0.1	-	-

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Table V-8, Continued

Element	Al	Be	Ca	Fe	K	Li	Mg	Na	Si	B	F	Cl
Final Product Tolerance	11 ppm	0.06	$2x10^3$	$2x10^3$	$1x10^3$	1.2	6	5.2	50	0.2	1.5	200
Reagent												
Nitric acid	$2x10^{-3}$	$4x10^{-5}$	$2x10^{-2}$	$4x10^{-2}$	0.5	$L2x10^{-4}$	10^{-3}	$4x10^{-2}$	$4x10^{-2}$	-	-	L5
Oxalic acid	1	$2x10^{-3}$	0.5	1.5	0.2	$2x10^{-3}$	$2x10^{-2}$	1	0.5	-	-	-
Perchloric acid	-	-	-	-	-	-	-	-	-	-	L0.3	13
Picrolonic acid	L5	$L5x10^{-2}$	L25	L50	-	0.255	5	50	L50	L0.1	-	-
Potassium dichromate(2)	10	-	L10	-	-	-	-	50	-	-	-	L10
Potassium permanganate	L20	$L5x10^{-2}$	L50	L100	-	L1	-	L90	L10	0.2	15	L10
Silver oxide	-	-	-	-	-	-	-	-	0.1	-	-	-
Strontium bromide	No analysis											
Strontium iodide	No analysis											
Sulfuric acid	$1.3x10^{-2}$	$7x10^{-5}$	$2x10^{-2}$	$5x10^{-2}$	-	10^{-4}	$2x10^{-2}$	0.2	$L10^{-2}$	$2x10^{-2}$	-	-

(1) Phosphorus in ammonium molybdate, 1.7 ppm; in iodine, L 1 ppm. Tolerance limit, > 350 ppm.

(2) Sulfur in hydrochloric acid, L 75 ppm; in barium metal, L 5 ppm; in iodine, L 20 ppm; in potassium dichromate, 50 ppm. Tolerance limit, 3000 ppm.

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CHAPTER VI

REFRACTORIES

USES FOR REFRACTORIES

In the metallurgy of plutonium there are three principal applications which require the use of special refractories. These are: (1) Liners for reduction bombs or other equipment in which the metal is reduced from a salt; (2) Crucibles for remelting the metal for purification and casting; and (3) Molds or investments in which the metal is cast. For experimental work a large variety of materials in the form of crucibles of many sizes and shapes has been involved. The sizes thus far have ranged from internal volumes of 0.1 to 15 ml. It is likely that other needs will develop such as pouring funnels, insulation, radiation shields and other furnace accessories.

The chemical and physical properties required in the refractory are entirely different in the three applications and a material which is perfectly adapted to one use may prove entirely unsuitable for another. The suitability of a given material to a given use can be determined only by actual experience. In the handling of a molten metal which is as reactive chemically as plutonium (same order of activity as cerium and magnesium), general metallurgical experience cannot point with certainty to a refractory which can be depended upon for any part of the job. Consideration of chemical stability, based upon thermodynamics, can eliminate a great many substances from consideration and indicate a fairly large list of compounds as possible candidates for further study and development.

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From this list must be eliminated those materials containing substantial amounts of such highly undesirable elements as lithium, beryllium, boron and fluorine, while others containing carbon, oxygen or any of the light metals must be avoided or regarded with suspicion until careful tests have established their acceptability.

Ceramic experience in the manufacture of crucibles for the melting of metals has not included any really comparable case. The use of clay as a bonding or plasticizing agent has been all but universal in the ceramic industries until quite recent times, but for the reduction or remelting of such active metals as uranium and plutonium any substantial amount of silica in the crucible is practically prohibited. Not only has it been necessary to manufacture crucibles from materials formerly unused for such purposes, but entirely new materials hitherto unknown even as laboratory curiosities have been discovered, their manufacture developed, and the materials made into the most satisfactory crucibles for melting plutonium.

Refractories for Metal Production

Liners for reduction bombs must be chemically inert toward reactants and products and must be capable of withstanding the thermal shock of the rapid heat evolution accompanying the reaction. In addition, other requirements may be necessary in special cases to fit the refractory to the special case. For example, if the salt to be reduced may reach its melting point before the reaction begins, then it is necessary to provide an impermeable liner to avoid loss of material by soaking into the pores. Again, if a given rate of heating of the reduction bomb is to be repeated on every run, the thermal conductivity of the liner must be reproducible;

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also, the rate of heat transfer from the bomb to the liner must be duplicable, hence the fit of the liner to the bomb must be controlled.

Since the best reducing agents are the alkali and alkaline earth metals, it is evident the bomb liner must be sufficiently stable to resist reduction by these elements. This means that it must be an alkaline earth oxide or sulfide or one of a very limited number of other compounds of comparable stability. Up to the present time the most successful substance of those which have been extensively tested for liner construction has been MgO.

It should be pointed out that when calcium is the reducing agent, any other oxide is likely to be reduced. In the case of MgO the result is not generally harmful since the magnesium produced is readily volatilized. If BeO or ThO_2 is the refractory, an appreciable contamination of the metal by Be or Th may occur. Contamination by oxygen seems less likely to occur during reduction than in subsequent remelting and casting, especially if the reductant is calcium. The possibility of oxygen pick-up could be substantially diminished by the use of sulfide liners, and the development of sulfide crucibles would seem to afford the best insurance against the possibility of serious difficulties from this source. To a lesser degree the same remarks might be applied to the development of nitride crucibles.

Refractories for Remelting

Crucibles for remelting and casting must be strong enough to hold together under the thermal conditions imposed, refractory enough to stand any superheating required (as for purification), and must not contaminate

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the metal with any objectionable impurities. This last requirement has led to intensive research programs on sulfide and nitride refractories. The extremely low tolerance limit for beryllium has also ruled out beryllia which otherwise would be a very useful refractory.

Questions have repeatedly arisen as to what purity specifications must be applied to refractory materials in order to assure meeting a given tolerance limit for a given impurity. Obviously, no general answer can be given since the distribution of an element between crucible and melt would vary with the element, the type of crucible, and the melting conditions. As a tentative basis for specifying the purity of refractory materials it has been necessary in many cases to make some sort of guess as to what the practical distribution would be. The result has been a number of raw material specifications in which the maximum light element impurity was placed at 50 times the tolerance level in the product. Thus, for a light metal whose tolerance limit is 0.2 ppm, the specification on ThO_2, for example, has been written tentatively as 10 ppm, maximum. Revision of such preliminary guesses on the basis of extensive analytical data will be necessary before completely satisfactory specifications can be written.

The use of oxide refractories for remelting plutonium is fraught with great uncertainty as to the amount of oxygen which will be dissolved in the metal. Plutonium forms several very stable oxides and it can therefore be expected to react with oxide crucibles, especially if superheating is employed, entering into reactions such as the following:

$$Pu\ (liq.) + ThO_2\ (s) = PuO_x\ (s) + Th\ (\text{dissolved in Pu})$$

or

$$Pu\ (liq.) + 2\ MgO\ (s) = PuO_x\ (s) + 2\ Mg\ (gas)$$

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The amount of oxygen which will be absorbed by the metal as a result of these or similar reactions will depend upon the solubility of the oxide in the metal or the ease with which the solid oxide is separated from the melt. No data are available on these questions but it seems obvious that complete freedom from suspended particles of oxide could never be assured under conditions which permit the occurrence of these reactions.

Analogy with other metal-oxide systems affords the only possibility of predicting the solubility of plutonium oxide in the metal. Uranium oxide is soluble in molten uranium to the extent of 30 to 200 ppm of oxygen. The oxides of zirconium and titanium are sufficiently soluble in the parent metals to render them completely non-ductile. If PuO_2 is reduced to PuO in the presence of the metal, it may be expected that this oxide is even more soluble in the metal. This analogy is drawn from the high solubilities of FeO and NiO in their respective metals which have been recorded as 1700 and 2000 ppm of oxygen, respectively, at the melting points. This line of reasoning leads to the conclusion that it is highly improbable that any oxide crucible can be obtained in which plutonium can be remelted without considerable oxygen contamination.

Considerations similar to the foregoing would rule out any carbide, boride or phosphide from consideration. This leaves only a rather limited number of types of substances whose melting points are high enough to place them in the category of refractories. Among these, the ones which have offered the most promise and which therefore have been most fully investigated are the nitrides, the sulfides, and a few pure metals.

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Refractory Molds for Castings

When molten metal is poured into a cold mold, solidification begins very rapidly and there is little opportunity for chemical reaction between the metal and the mold. In the casting of small metal objects whose surfaces must be smooth and unwrinkled it is frequently necessary to heat the mold to some temperature approaching the melting point of the metal. This retards solidification so that the mold may be entirely filled before freezing begins, thus avoiding "cold shuts", "splashes" and other surface defects. At the same time it offers greater opportunity for reaction of metal and mold, and necessitates the use of more or less inert materials for mold making.

In the investment method of casting, the refractory in the form of semi-fluid mixture is poured around a fusible pattern, the latter being then melted out after the mold has hardened. No experiments have as yet been performed with plutonium.

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REFRACTORY SUBSTANCES AND THEIR PROPERTIES

General Considerations

Of the many properties that must be considered in choosing the proper material for a refractory problem, the first to be considered are melting point and stability. If the refractory is to be used at temperatures as high as 1500°K., the types of possible refractory compounds can be limited on the basis of melting points and stabilities to six classes of substances, namely: high melting elements, borides, carbides, nitrides, oxides and sulfides. Practically all silicides, phosphides, fluorides and similar analogues can be eliminated because of instability of the solid compounds.

Except for carbon, the only elements that would be considered will be found among the transition metals ranging from the fourth subgroup to the eighth. Among the five groups of compounds to be considered, stability will be found to be a more important criterion than melting point.

Volatilities of the promising borides, carbides, nitrides and sulfides are due to their decomposition to the elements, since none of these refractory compounds is believed to exist undecomposed in the vapor phase at the high temperatures required for sintering. Therefore, the least volatile compounds will be the most stable compounds and from heats of formation one can predict which compounds would be suitable.

Stability of Refractory Substances at High Temperature and Low Pressure

As a summary of the stability of the refractories toward vaporization, the stable refractories will be listed for the three temperatures 2500°K., 2000°K. and 1500°K. Since vacuum is usually preferable to inert gas because it is so difficult to obtain a pure inert gas, a

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material with a vapor pressure greater than 10^{-3} mm. or 10^{-6} atm. will be considered rapidly volatile. In a vacuum, a material with a vapor pressure of 10^{-6} atm. will evaporate at a rate of about 0.03 mm. thickness per hour. Any greater rate of vaporization would be excessive with the wall thicknesses usually used if the sintering time is long. Compounds not listed are unstable.

Elements.--

2500°K. - Ta(10^{-10}), W(10^{-10}), Re(10^{-9}), Os(10^{-8}), Hf($2x10^{-8}$), Ir($2x10^{-8}$), and Cb($2x10^{-8}$ atm.) are nonvolatile or slowly volatile. C(10^{-7}), Ma($6x10^{-7}$), Ru($6x10^{-7}$), and Mo($7x10^{-7}$ atm.) are moderately volatile. All other metals are rapidly volatile.

2000°K. - Ta, W, Re, Os, Hf, Ir, Cb, C, Ma, Ru, Mo, Zr, Th, Rh, Pa and Pt are nonvolatile.

1500°K. - In addition to those listed at 2000°K., Ti, Y, Pd, Co, Ni, Sm, and Sc are nonvolatile. Fe is moderately volatile.

Borides.--

2500°K. - ZrB, HfB, ThB, CbB, TaB and WB are probably the only borides with less than 10^{-6} atm. pressure.

2000°K. - In addition to those at 2500°K., Ti, Mo, U and carbon borides are nonvolatile.

1500°K. - The rare earth borides would be added to those listed at 2000°K.

Carbides.--

2500°K. - ZrC, TiC, HfC, ThC_2, CbC, TaC, Ta_2C, MoC and tungsten carbides are nonvolatile.

2000°K. - The uranium carbides, YC_2, VC, SiC and B_6C are nonvolatile in addition to those listed at 2500°K.

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1500°K. - Cr_3C_2 and the rare earth carbides would be added to those at 2000°K.

Nitrides.--

2500°K. - HfN and ZrN with equilibrium pressures of 10^{-5} atm. of N_2 are rapidly volatile to form N_2 and solid metal and the nitrides of Pa and Th are probably even more unstable. All other nitrides are even more unstable.

2000°K. - HfN, ZrN, PaN and Th_3N_4 are nonvolatile. UN, TiN and YN have vapor pressures greater than 10^{-6} atm. and are rapidly volatile. Other nitrides are even more unstable.

1500°K. - HfN, ZrN, Th_3N_4, PaN, UN, TiN, rare earth nitrides, TaN, CbN and ScN are stable and nonvolatile. All other nitrides are unstable.

Oxides.--

2500°K. - ThO_2 (10^{-6} atm.) is moderately volatile. Y_2O_3 (10^{-5}) and UO_2 (10^{-5} atm.) are rapidly volatile. All other oxides are even more volatile.

2000°K. - ThO_2 (10^{-9}), Y_2O_3 (10^{-8}), UO_2 (10^{-8}), HfO_2 (10^{-7}), and ZrO_2 (10^{-7} atm.) are nonvolatile. CaO ($5x10^{-7}$), La_2O_3 (10^{-6}), BeO (10^{-6}) and MgO (10^{-6} atm.) are moderately volatile. Sc_2O_3 ($5x10^{-5}$), Ce_2O_3 ($5x10^{-5}$), Al_2O_3 (10^{-5}), Ti_2O_3 (10^{-5}) and SrO (10^{-5} atm.) are rapidly volatile.

1500°K. - ThO_2, Y_2O_3, UO_2, HfO_2, ZrO_2, CaO, rare earth oxides, BeO, MgO, Sc_2O_3, Ti_2O_3, SrO, BaO, CbO_2 and TaO_2 are nonvolatile.

Sulfides.--

2500°K. - ThS is moderately volatile and CeS is rapidly volatile.

2000°K. - ThS and Th_2S_3 are nonvolatile. CeS (10^{-7} atm.) and Ce_3S_4 are slowly volatile. US is moderately volatile and BaS is rapidly volatile.

1500°K. - ThS, Th_2S_3, Th_7S_{12}, CeS, Ce_3S_4, US, U_2S_3, Hf_2S_3, Zr_2S_3 and BaS are nonvolatile. The rest of the rare earth sulfides as well as sulfides of Cb, Y and Sc could also be included.

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Physical Properties of Refractories of Interest

Some of the physical properties of those substances which seemed promising as refractories in the metallurgy of plutonium are listed in Table VI-1.

Table VI-1. Properties of Refractories

	Density 25°C.	Melting Point °C.	Linear Coefficient of Expansion (500-1000°C.)	Thermal Conductivity cal/cm/sec/deg.C.	
				25°C.	1000°C.
BeO	3.0	2550°C.	10×10^{-6}		.01
MgO	3.6	2650°C.	12×10^{-6}	.05	.02
CaO	3.35	2710°C.	14×10^{-6}		
La_2O_3	6.5	2350°C.	10×10^{-6}		
ZrO_2	5.5	2715°C.	8×10^{-6}	.004	.004
$ZrSiO_4$	4.7	d. 1650°C.	4×10^{-6}		.009
ThO_2	9.7	3050°C.	11×10^{-6}		.003
Ce_3S_4	5.3	1840°C.		semi-metallic	
CeS	5.93	>2200°C.		metallic	
Th_7S_{12}	7.78	1770°C.		semi-metallic	
Th_2S_3		2000°C.		metallic	
ThS	9.56	>2200°C.		"	
TiN	4.8	2950°C.		"	
ZrN	6.97	3000°C.		"	
UN	14.31	2630°C.		"	
ZrC	6.5	3500°C.		"	
TiC	4.1	3150°C.		"	
TaC	14.0	3900°C.	8×10^{-6}	"	
Mo	10.2	2600°C.	7×10^{-6}	.33	.2
W	19.2	3380°C.	4×10^{-6}	.39	.26
Ta	16.65	2996°C.	7×10^{-6}	.13	
Re	21.0	3170°C.			

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No specific heat data are available except for metals and oxides. The following equations can be given for the molal heat capacity as a function of temperature.

BeO	C_P =	$8.69 + 3.65\times10^{-3}T - 3.13\times10^{5}T^{-2}$
MgO		$16.68 - 0.40\times10^{-3}T - 135T^{-1/2}$
CaO		$10.00 + 4.84\times10^{-3}T - 1.08\times10^{5}T^{-2}$
ZrO_2		$11.62 + 10.46\times10^{-3}T - 1.777\times10^{5}T^{-2}$
ThO_2		$24.08 - 0.66\times10^{-3}T - 158.7T^{-1/2}$
Mo		$5.69 + 1.88\times10^{-3}T - 0.503\times10^{5}T^{-2}$
W		$5.65 + 0.866\times10^{-3}T$
Ta		$5.91 + 0.99\times10^{-3}T$
Re		$5.73 + 1.23\times10^{-3}T$

In Table VI-2, the free energies of formation are given in kilocalories per atom of O, S, N or C. The free energies at 1000°K. are given for the solid or liquid metals as standard states. The free energies at 1500°K. are first given for the solid or liquid metal states and then for the gaseous metals at one atmosphere for metals which are appreciably volatile. In all cases the standard states of the non-metals, oxygen, sulfur and nitrogen are the gaseous diatomic molecules.

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Table VI-2. Free Energies of Formation

	-ΔF of formation in kilocalories		
	1000°K.	1500°K.	1500°K. (gaseous metals)
BeO	125	113	148
MgO	121	108	106
CaO	127	115	120
La_2O_3	140	128	155
ZrO_2	110	100	
ThO_2	128	117	
CeS	120	105	118
Ce_3S_4	105	95	105
TiN	59	49	104
ZrN	60	49	
ZrC	56	67	
TiC	55	52	107

GENERAL METHODS FOR REFRACTORY MANUFACTURE

Treatment of Raw Materials.-- In general, the refractories used in this work have been made from raw materials of high purity. Chemical specification, however, is not the only criterion since the physical state is of equal importance. Oxides or carbonates in a light, fluffy condition would shrink so greatly on firing that distortion and cracking would inevitably result. Hence, pre-calcining or, in some cases, pre-fusion of the material is necessary.

Crushing and grinding must be done in mills which do not contaminate the product and in view of the hardness of most refractories this is not

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always simple. Acid washing of the ground material is rarely feasible. Control of grain size is of great importance, not only in the size range covered by screen analyses but in fine grain sizes requiring sedimentation methods. The blending of prepared batches of known grain size distribution is frequently necessary for maintenance of uniformity.

Mixing.-- In the refractory mix there will often be several ingredients which must be mixed together, and the thoroughness with which this is done determines to a great extent the uniformity of the finished product. In the case of organic bonds and lubricants added to non-plastic materials it will be found in most cases impossible to produce a fine grain size in the mixing operation because the mass tends to accumulate in balls or larger masses. In order to provide a mix suitable for pressing, it must be disintegrated by putting it through a coarse screen or one of several types of mechanical disintegrator which will produce a granulated mix for accurate pressing.

Forming Methods.-- The majority of refractories at present are made by the so-called dry press method where a mix containing around 8 per cent of water is pressed in a steel mold under high pressures from 5000 to 100,000 psi. This method has the advantage of giving an article a true shape, reasonably uniform structure and high density. The method, however, has limitations when the article is complicated in shape or large in size because of the difficulty in getting a uniform distribution of pressure over the volume. For this reason many of the larger refractory shapes are rammed with a hand tool or air hammer into the mold, using a mix of much the same consistency as for pressing. If carefully done this gives a molded article having a fairly uniform structure throughout,

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but if carelessly done the density will vary from point to point and cracks are apt to develop in firing.

Another method of forming articles is to cast a fluid suspension of the finely ground raw material in absorbent molds made of plaster or porous clay. In the case of non-plastic refractories, a suspension can usually be formed if the particle size is sufficiently fine and the pH of the suspension is properly adjusted. However, the cast is lacking in strength when green, and when dry it is much more difficult to handle than plastic clay bodies.

Drying.-- The drying operation is a very critical step in the manufacture of bodies in which organic materials such as waxes or stearates are used as lubricants or bonds. These must, of course, be removed before the firing operation and in this case a carefully controlled firing schedule and atmosphere schedule is necessary to remove the organic materials without rupturing the structure.

Firing.-- Many of the oxides may be fired in a high frequency induction furnace with a graphite lining which enables temperatures up to 2500°C. to be readily attained. Other oxides which are reduced under such conditions may be fired in a vacuum or an inert gas by using a molybdenum, tantalum or tungsten shield in a high frequency furnace. It is also possible to obtain temperatures of 2000°C. or above in combustion fired furnaces either by the use of oxygen or by the use of highly preheated air. The best furnace for a given refractory requires considerable study of the problem.

Testing of Fired Product.-- The properties considered most essential in the finished product were: (1) a smooth surface,

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(2) a surface of high density or free from porosity, (3) a high density for the entire body, (4) sufficient shrinkage to bond and to produce high density, and (5) uniformity of size and shape and absence of deformation.

The surface condition was estimated by feel and by visual observation. The porosity of the ware was defined in percentage as

$$\frac{\text{Volume of Voids}}{\text{Total Volume of Crucible}} \times 100 = \text{Per cent Porosity}$$

The volume of the voids was measured by determining the volume of trichloroethylene absorbed on soaking the body until no further absorption occurred. Another useful method for estimating the surface porosity of crucibles is to immerse them in a solution of a suitable dyestuff, remove the excess, and then note the residual color due to the amount of the dyestuff absorbed.

Shrinkage was defined as

$$\frac{\text{Outside Diam. after Heating}}{\text{Inside Diam. of Mold}} \times 100 = \text{Per cent Shrinkage}$$

Proper dimensions in the finished ware were obtained by experimentally determining the shrinkage under the desired firing conditions and then constructing forms, mandrels and dies of the proper over-size to allow for shrinkage. Deformation was prevented by varying the composition of the mix in various parts of the body or by varying the pressure applied to different parts if die-pressed. The above empirical definitions for "Per cent Porosity" and "Per cent Shrinkage" do not represent true porosity or true linear or volume shrinkage, respectively. The defined "Per cent Porosity" is a useful measure of surface porosity, and the defined "Per cent Shrinkage" is useful for designing dies for pressing crucibles so that the finished ware will have the desired dimensions.

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Beryllia

Casting Method.-- The beryllia used was of the "high fired" grade and varied considerably from different sources. A satisfactory batch analyzed as follows: SiO_2, 3.20; Fe_2O_3, 0.02; Al_2O_3, 0.80; CaO, 0.01; MgO, 0.01; and BeO (by difference), 95.96 per cent.

The beryllia casting slip was prepared by milling with water in a one gallon steel ball mill. After milling the iron was removed by washing three times in commercial HCl, then with water three times. The efficiency of the treatment was checked by a KSCN indicator. The specific gravity of the slip varied between 1.55-1.65, depending on the size of article to be cast. The particle size distribution is shown in Table VI-3.

Table VI-3. Particle Distribution of Beryllia Casting Slip

Particle Size in Microns	% Finer Than
100	100
30	100
10	98
3	64
1	16
.3	4

The slip was cast in plaster molds using regular pottery technique. The casting time was short - 2 to 45 seconds - depending on the wall thickness desired. The ware was fired in a gas fired furnace from 1500° to 1900°C., depending on the porosity desired. The linear firing shrinkage was as follows: at 1500°C., 6 per cent; at 1850°C., 19 per cent. The porosity at 1850°C. was 0 to 2 per cent.

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Pressing Method.-- This process was carried out like wax pressing magnesia except 10 per cent of emulsified paraffin was used instead of carbowax. For firing porous crucibles, a temperature of 1700°C. was sufficient. The particle size distribution was the same as for the casting mix.

For crucibles of zero porosity the same procedure was followed except that 3.4 per cent CaO (as whiting) was added in the ball mill.

Magnesia

Magnesia Molding Technique by Vibrating.-- The fused magnesia used had the chemical analysis shown in Table VI-4 and a grain size distribution as shown in the first column of Table VI-5.

Table VI-4. Chemical Analysis of G.E.S.A.Grade Magnesia

SiO_2	4.23%
CaO	1.27
Fe_2O_3	.07
Al_2O_3	.10
MgO (by difference)	94.23

Table VI-5. Particle Size Distribution of Magnesia

	Per Cent Finer Than		
Size in Microns	As Received	2 Hour Milling	6 Hour Milling
300	100	100	
100	30	76	100
30	5	32	80
10		10	44
3		2	16
1		0	5

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Crucibles were molded by filling the cavity provided in the mold assembly with the dry mix while it was vibrated. This action was continued until there was no more reduction in volume. One hundred grams of the prepared mix could be vibrated into 39.0 ml. volume. The center pin was then withdrawn and 13 per cent by weight of water was added by slow dripping through the hole and the top hopper. After 3 to 4 hours the material was uniformly saturated and the mandrel was withdrawn. The outside shell was then removed and the crucible placed in the dryer. Four hours at 100°C. was found adequate for complete drying.

Dry crucibles were fired in an induction furnace with a graphite liner. The temperature was raised to the maximum temperature as quickly as convenient and then held for a predetermined time. A typical schedule was to reach 2000°C. in one and one-half hours and to hold that temperature for twenty minutes. Linear shrinkages and porosities of ware fired at three temperatures are given below:

	1800°C.	2000°C.	2300°C.
Per cent linear firing shrinkage	1	3.3	5.0
Per cent porosity	30	26.0	16.1

Magnesia Molding Technique by Ramming.-- The material shown in the last column of Table VI-5 was mixed with 5 per cent of water and then screened through a 20 mesh sieve and the water introduced by hand kneading; it was then screened twice through a 10 mesh sieve. The powder was added to the mold in small increments and was hand tamped using a tool 3/4 in. wide with teeth cut in it. When the top of the crucible was reached, a larger blunt half-inch diameter tool was used until about one-eighth inch extra material had been tamped in and a cutter head was

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then inserted in the top to level it off. A solid plug was then inserted and pounded a few blows with a mallet, or the mold was squeezed in a press. This finished the bottom and completed molding. Air hammers can also be used to give denser structures. Firing was done in an induction furnace which required 2¼ hours to reach 1750°C. The temperature was held 30 minutes. The firing shrinkage was about 7 per cent and the porosity 20 per cent.

Magnesia Casting Technique.-- Fused magnesia was ball milled in a porcelain mill with absolute alcohol to produce a slip of 2.3 specific gravity. The Fe_2O_3 content after milling was 0.07 per cent and the SiO_2, 0.16 per cent. The casting was carried out in plaster molds using ordinary pottery technique. The drying shrinkage was small and drying, after removal from the mold, had to be carried out slowly in a closed chamber to prevent cracking. Firing was carried out in graphite in the induction furnace. At 1850°C. the shrinkage was 7 per cent and the porosity 0.5 to 4 per cent. At 2100°C. the ware became highly translucent and the porosity was zero.

Magnesia Molding by Wax Pressing.-- Magnesia of the grain size shown in the last column of Table VI-5 was mixed with 12 per cent of water soluble wax or paraffin emulsion and pressed in a steel mold to a pressure of 40,000 psi. Only the small size crucibles have been made satisfactorily in this way. Controlled porosities ranging from 0 to 15 per cent are obtainable in small crucibles.

Calcium Oxide

Calcium oxide is obtainable in considerable purity commercially as certain grades of lime or it can be readily prepared in a very pure state chemically.

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Types of Calcium Oxide Investigated.--

1. Ste. Genevieve Lime. A commercial kiln-burned high calcium lime of special purity.

2. "Sintered" Lime. Prepared by sintering Ste. Genevieve lime in a graphite crucible by induction heating at 1600°C., followed by grinding in a Micropulverizer to -200 mesh.

3. "Fused" Lime. Made by actually fusing Ste. Genevieve lime in an electric arc, followed by crushing in a jaw crusher and grinding in a Micropulverizer to -200 mesh.

4. "Pure" Lime. Prepared by treating distilled calcium with distilled water, drying the precipitated hydroxide and igniting in graphite crucibles by induction heating. The ignited product was ground in a Micropulverizer to -200 mesh. The extent of calcination was about equivalent to that of "sintered" lime but the particle structure was not the same.

Methods of Fabrication.-- The following procedures offered promise and were investigated:

1. "Slip casting" from non-aqueous media such as absolute alcohol. No good slips were obtained and the investigation was discontinued.

2. "Hand tamping" in a graphite mold with a mandrel by jolting on a hard surface by hand.

3. "Mechanical jolting" which consists of tamping in a graphite mold with a mandrel on a pneumatic mechanical jolting table.

4. "Die pressing" in a three-way split die of hardened die steel with a punch at pressures in the range 10,000 to 50,000 psi.

Firing of Ceramic Bodies of CaO.-- The only satisfactory mode of firing calcium oxide bodies in the temperature range 1600° to 2200°C. was

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by induction heating. However, methods of supporting and protecting the ware during firing and the influence of the duration and temperature of firing on properties presented problems for investigation.

Graphite heaters, surrounded by carbon insulation, were used throughout. Reaction between CaO and graphite at 1650°C. necessitated the separation of these materials when heated at or above that temperature. In the various types of tamped crucibles this condition required the firing of the body in the graphite crucible at 1600°C. during which heating some shrinkage occurred, the removal of the partially sintered lime crucible from the graphite, and a second heating in a larger graphite crucible. In this second heating the lime crucible was separated from the bottom of the graphite crucible by supporting it on a less active material such as uranium carbide, zirconium carbide, or even magnesia which does not tend to react with graphite as readily as does calcium oxide. Shielding from the graphite, loose carbon dust and gases containing carbon was necessary to prevent blackening and carburization. Magnesia was found to constitute the best shields. Altogether, firing at temperatures from 1600° to 2200°C. were investigated, and firing times from the time required to reach a specified temperature to holding one hour at temperature were studied.

Effect of Mode of Calcining Lime.-- Commercially burned lime with no further treatment did not produce ware of sufficient uniformity or density to be useful when fabricated by hand tamping. In die pressing, however, some fairly good ware was obtained from such lime.

The results obtained with the specially prepared limes described above, fabricated by hand tamping and double fired, were as follows:

Refractory	Porosity	Shrinkage
"Sintered" lime	9.1%	7.4%
"Fused" lime	15.8	3.4
"Pure" lime	11.9	7.4

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It had been expected that maximum density might be obtained with fused lime since maximum change in crystal structure has occurred. Actually, ware made from fused lime has least density and little strength because of the fact that all change has already occurred on fusion and there is no further change or shrinkage on firing the body. The very pure lime lacked cohesion and hence was fragile. The sintering of eutectics of lower melting point with small amounts of impurities in the commercial lime was doubtless responsible for the greater density and mechanical strength of ware made from such lime. This suggested the addition of various oxides to lime for this purpose with the excellent results described below.

Effect of Firing Temperature.-- The optimum temperature of firing was investigated from 1600° to 2200°C. The optimum temperature varied with time of firing and with bodies formed by different procedures but in general maximum shrinkage had been achieved on heating to 2100°C. and holding for 15 minutes at that temperature. Porosities of 20 to 30 per cent in hand tamped material fired at lower temperatures dropped to 1 to 5 per cent under these conditions.

Effect of Die Pressing.-- The greatest improvement in the fabrication of CaO ware was obtained by die pressing. Pressures of 10,000 to 50,000 psi were used at different points on various models. For instance, a pressure of 50,000 psi was applied to the sides of a large crucible with a pressure of 23,000 psi on the bottom.

Effect of Admixture of Other Oxides with Lime.-- The use of other less basic oxides with CaO for crucible material was investigated. SiO_2, ThO_2, ZrO_2, Al_2O_3 and BeO were added to lime in varying proportions. The density was improved most by one to two per cent of

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BeO, Al_2O_3, or TiO_2, the porosity being decreased from 10 to 20 per cent in lime alone to less than 1 per cent in these mixtures. Five per cent or more of these added oxides tended to produce cracking and blistered surfaces. Silica up to 2 per cent produced little effect, but 5 per cent silica decreased the porosity from about 15 per cent to 3 per cent. Magnesia produced no observable effects until about 30 per cent was added, on which some decrease of porosity occurred.

Use of Lubricants and Binders.— The use of paraffin as a binder and lubricant was found to be somewhat helpful, although it is not as beneficial as is its use with silicates. Water solutions and suspension of waxes and binders being impossible with calcium oxide, paraffin dissolved in carbon tetrachloride was used. A thick paste of lime in the solution of paraffin in CCl_4 was prepared by grinding; the solvent was evaporated and the resulting mass granulated. The granular material was then fed into the dies for pressing. Some increase in density was gained on using up to 10 per cent by weight of paraffin, but over 10 per cent caused an increase in porosity of the ware.

Other Oxides and Mixtures

Uranium Dioxide.-- Commercial UO_2 can be pressed into crucible form by using some material such as paraffin wax or sodium silicate as a bonding material. Without some bonding material it was found impossible to form a crucible, using pressures up to 70,000 psi, that was sufficiently well bonded to withstand handling. A very satisfactory bond is obtained by using 0.5 to 1.0 per cent sodium silicate and using a pressure of 50,000 psi, the sodium silicate being added as a 40° Baume solution

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containing approximately 35 per cent solids. A fairly good bond was attained by using 0.5 to 2 per cent paraffin wax, at 50,000 psi; however, the bond was not sufficiently strong to withstand handling when a large crucible was pressed at 45,000 psi.

Smaller crucibles were pressed using both wax and sodium silicate, and fired in the induction furnace to approximately 1750°C. and to 2000°C. in a graphite container under vacuum. At 1750°C. the crucibles containing sodium silicate were a dull brick red color and fairly well sintered, while crucibles containing paraffin were of the same color and poorly sintered. At 2000°C. the crucibles containing silicate were very well sintered, the surfaces being smooth and a dark gray to black in color. A cross section of the crucibles when ground and polished gave a bright metallic surface.

Considerable shrinkage takes place when the crucibles are fired to 2000°C. The following measurements were made on small crucibles in which 0.925 per cent silicate was used as a binder.

Diameter of crucible after pressing: 0.755 in.

Total Pressure Used	Diam. after Sintering at 2000°C.
14 Tons	0.700 in.
10 "	0.697 "
7 "	0.695 "

The porosity, as measured by determining the amount of trichloroethylene adsorbed after 10 minute submersion, was found to be approximately 20 per cent. Crucibles thus far produced were fired to 2000°C. and immediately allowed to cool. The entire heating operation was carried out in approximately 45 minutes.

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Crucibles have been prepared by tamping and firing the oxide in graphite forms, but these crucibles were extremely porous and not suited for any use. Crucibles fired in a graphite container without a vacuum were not oxidized to U_3O_8 and a well sintered, smooth surfaced crucible was produced.

Thorium Dioxide.— Calcined or fused thoria was ground and acid treated as described for preparing beryllia. A slip of 2.0 to 2.5 specific gravity was made up and cast in plaster molds as for beryllia. Firing was carried out in a combustion furnace. At 1850°C. the linear shrinkage was 7 per cent and the porosity 25 per cent. The fired crucible had a clear bell-like ring, more resonant than metals, but gradually lost it with time.

Mixtures.— Oxide mixtures giving no porosity when fired at about 1700°C. in a combustion furnace are listed below. All of these materials were ball milled, pressed in steel molds and then fired.

Composition	Firing Temperature	Per cent Shrinkage
MgO - 99. $Ca_3(PO_4)_2$ - 1.	1700°C.	6.8
MgO - 98. $Ca_3(PO_4)_2$ - 2.	1700°	7.0
MgO - 95. $Ca_3(PO_4)_2$ - 5.	1550° 1700°	
MgO - 90. ZrO_2 - 10.	1700° 1740°	8.0 - 9.0
MgO - 91. TiO_2 - 9.	1700° sl. overfired	11.5
MgO - 40. CeO_2 - 60.	1530°	12.5

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Composition	Firing Temperature	Per cent Shrinkage
MgO - 97.0 CaO - 1.5 BeO - 1.5	1700°	9.3
MgO - 95.0 CaO - 2.5 BeO - 2.5	1550°	7.3
MgO - 90. CaO - 5. BeO - 5.	1500°	8.0
BeO - 95. CaO - 5.	1700° 1740°	6.9
ThO_2 - 99.5 CaO - 0.5	1700°	16.

SULFIDE REFRACTORIES

The primary consideration leading to the study of sulfides as refractories was originally the large tolerance for sulfur (3000 ppm) compared with the low tolerances for the light elements present in refractories of the ordinary type. Aside from the requirement of high purity, the sulfide refractories are of value because they have properties favorable for proper grinding, pressing (with or without binders), and sintering into the final crucible.

After consideration of known and estimated characteristics such as resistance to reduction, melting point and volatility, investigations were begun on the sulfides of barium, cerium, thorium and uranium, which were chosen as representative of the most promising metals. The actual compounds that have been prepared and studied are: BaS, CeS, Ce_3S_4, Ce_2S_3, ThS, Th_2S_3, Th_7S_{12} (or Th_4S_7), ThS_2, US, U_2S_3 and US_2. In

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addition to the above pure substances, certain "mixed crystals" and other phases of variable composition have been studied. These include solid solutions of CeS, ThS and US in each other and the sulfide of the type MS derived from "Misch metal" and indicated as MiS.

Preparation of Sulfides

There are three general methods that have been used to prepare the sulfides: Method I - By the treatment of the oxide with H_2S in a carbon system with subsequent vacuum heating in the case of intermediate sulfides. Method II - By the action of the correct amount of H_2S upon the metal hydride, followed by high temperature vacuum heating to obtain a uniform product. Method III - By the reduction of the higher sulfide by the metal hydride, the higher sulfide having been prepared by the first method.

If anhydrous halides were available, the higher sulfides could also be prepared by the action of sulfur or hydrogen sulfide, or both, upon the halide.

Reaction of Oxides with H_2S (Method I).-- The starting oxide material is ground as fine as possible (around 325 mesh) and is lightly tamped into a graphite container with holes left in the powder for the graphite tubes through which the H_2S gas is introduced. All hot material in the system should be made of carbon or graphite so that oxygen cannot be introduced by attack of oxide refractories. Porous carbon and carbon black are used as insulating materials. The graphite container can be used as heating element if induction heating is used, or carbon elements can be used for resistance heating.

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In the first stages of conversion of oxide to oxysulfide, the hydrogen sulfide will be converted to water. As the temperature is raised to complete the conversion of the oxysulfide to sulfide, the hydrogen sulfide will attack the carbon tube and carbon parts to form CS which reacts with the oxysulfide to form sulfide and CO. The important point in obtaining complete conversion is to keep the temperature low enough to prevent sintering of the powder. Until the oxysulfide has been largely converted, the temperature should be kept appreciably below the eutectic point between the oxysulfide and the sulfide. If the powder sinters, the gas cannot penetrate it for reaction. After the oxysulfide is largely converted so that there is no longer danger of eutectic melting, the temperature is raised to remove the last traces of oxygen. If the conversion has not been completed due to sintering or other reasons, the powder is ground to 100-200 mesh and reheated in H_2S. The individual details in the preparation are given under each compound prepared by this method.

Ce_2S_3 - This sulfide is one of the most difficult to prepare because of the existence of a very low eutectic melting point between Ce_2S_2O and Ce_2S_3. There is also an oxysulfide Ce_2SO_2. The starting material is CeO_2 which is heated just below 1200°C. until hydrogen sulfide corresponding to more than twice the theoretical amount has been passed over. Then the temperature is slowly raised to 1300°C. with a short heating as high as 1400°C. required for a very oxygen-free sample.

Ce_3S_4 - This sulfide is readily prepared by heating the Ce_2S_3 prepared from the oxide in a vacuum better than 10^{-4} mm. Hg at 1900° to 2000°C. for several hours. Molybdenum containers are used to contain the molten sulfide. If the temperature is allowed to rise too high or

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if the container is too full the surface tension of the molten sulfide is low enough so that it will rise over the lip of the container and thus decrease the yield.

ThS_2 - The starting material is ThO_2. There is only one oxysulfide, the yellow ThOS. The eutectic points are all high and there is not much trouble due to melting, but a higher temperature is required for conversion than in the case of Ce_2S_3. The ThO_2 is heated just below 1300°C. until more than twice the theoretical amount of H_2S has been passed over and the temperature is then slowly raised to 1500°C.

Th_7S_{12} - This compound is prepared from ThS_2 exactly as Ce_3S_4 was prepared from Ce_2S_3.

US_2 - The starting material is U_3O_8, with about the same preparation conditions as for Ce_2S_3. Since there is partial decomposition to U_2S_3 at the higher temperatures, the temperatures must be lowered for some time after removal of the oxygen if US_2 is desired.

U_2S_3 - This sulfide can be prepared from US_2 exactly as Ce_3S_4 was prepared from Ce_2S_3.

BaS - The starting material is $BaSO_4$. The conditions are the same as for Ce_2S_3 except that a final temperature of about 1500°C. is required for complete conversion.

Reaction of Hydrides with H_2S (Method II).-- The apparatus for preparing sulfides by the action of H_2S upon metal hydride consists of a closed system of large volume into which known amounts of H_2S can be introduced. The reaction bulb is a long-necked flask with standard joint which is degassed in vacuum at 500° to 600°C. until a pressure of 10^{-5} mm. can be obtained at 500°C. The vacuum is broken with He and a

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piece of thorium or uranium metal is introduced into the bulb. The system is then evacuated and hydrogen introduced. To start the hydriding reaction, thorium is heated to 400°C. and is then maintained at 275°C. until hydrogen absorption is complete. This requires about 12 hours per 300 grams of thorium hydride. The temperature is then lowered to room temperature with further absorption of hydrogen to go from ThH_2 to $ThH_{3.5}$. Uranium is hydrided at 275°C. and goes directly to UH_3. After hydriding is complete, the system is cooled and evacuated. A known amount of hydrogen sulfide is introduced and the bulb heated to 450° to 500°C.

The final product is not homogeneous unless the highest sulfide has been prepared and must be heated in vacuum to obtain a homogeneous product. The material is heated at a low temperature until the hydrogen in the material has been all removed and is then heated to 1800° to 1900°C. in vacuum.

Reduction of High Sulfide by Metal Hydride (Method III).-- The higher sulfide is prepared by Method I from the oxide, and the metal hydride is prepared as described under Method II. In the case of cerium, the hydriding reaction takes place spontaneously at room temperature, although a slight heating with a burner is sometimes used to start the reaction more quickly. A large amount of heat is evolved and the Pyrex glass can actually be melted if the bulb is insulated. The hydride formed is CeH_3.

The higher sulfide and metal hydride are ground in propane to 50 mesh or finer. Since both the higher sulfide and metal have considerable amounts of impurities which distill out during the preparation, the purity of the samples must be known or a trial run made to determine the correct ratios to use to obtain the desired sulfide. All mixtures containing

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metal hydride and handled in a propane atmosphere. The mixture of higher sulfide and metal hydride powders is heated in a molybdenum crucible which is insulated by one turn of 0.002 inch Mo foil and a zircon crucible serving as a radiation shield. Induction heating is used with the Mo crucible serving as heating element. The reduction takes place in the vacuum system. After a vacuum of 10^{-5} mm. has been obtained, the diffusion pump is turned off and the preparation is heated with the coils low in order to keep the temperature down. The heating is continued at a low rate until practically all of the hydrogen has been evolved from the hydride. Rapid heating causes spraying of the hydride. When the hydrogen has been evolved, the diffusion pump is started to obtain a good vacuum and the preparation is heated to 1400°C. for 30 minutes in the case of cerium sulfide preparations and to 1500°C. for thorium or uranium preparations. Then the temperature is raised to 1700° to 1800°C. for 30 minutes to obtain a homogeneous product and to distill out impurities such as iron, oxygen, alkali and alkaline earth metals and others. The pressure is considerably better than 10^{-4} mm. at all times during the vacuum heating. At high temperatures the sintered sulfide preparation supplements the heating of the Mo crucible in the induction field when the preparation is one of the highly conducting sulfides such as CeS, ThS or US. The following sulfides have been prepared by this method:

CeS and Ce_3S_4	are prepared from Ce_2S_3 and CeH_3
*MiS	is prepared from Ce_2S_3 and MiH_3
$Ce_{2/3}Th_{1/3}S$	is prepared from Ce_2S_3 and ThH_3
ThS, Th_2S_3, Th_7S_{12}	are prepared from ThS_2 and ThH_3
$Ce_{1/2}Th_{1/2}S$	is prepared from ThS_2 and CeH_3

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$Th_{1/2}U_{1/2}S$ is prepared from ThS_2 and UH_3

US and U_2S_3 are prepared from US_2 and UH_3

*The symbol Mi is used to represent Misch metal.

Of the three methods, the method best suited for any particular compound depends mostly upon the material and equipment available.

Properties of the Sulfides

BaS - Pure BaS is white and has a density of 4.2. It has the NaCl crystal structure with a Ba-S distance of 3.2A. The melting point is above 2200°C., but it becomes appreciably volatile at 1600°C. with a vapor pressure of about 10^{-3} mm. It vaporizes due to decomposition to Ba and S gases. Barium sulfide can be machined or filed. It is soluble in water and reacts with moist air to give off H_2S. When well sintered it does not react as readily, but there is still noticeable reactivity. It is an electrical insulator with a specific resistance of above 1,000,000 ohm-cm. The molal free energy of formation at room temperature is given as -101.3 kilocalories.

CeS - It has a yellow metallic brass color and a density of 5.93. The NaCl crystal structure has a Ce-S distance of 2.88A. The melting point is above 2200°C. and it becomes appreciably volatile at 1900°C. with a vapor pressure of about 10^{-3} mm. due to decomposition to Ce and S gases. The presence of 1 per cent of Ce_3S_4 lowers the melting point sufficiently to give dense sintered material at 1850° to 1900°C. after 30 minutes; 2 per cent lowers the sintering temperature another 100°C. The well sintered CeS can be machined, filed or polished like a metal. It does not react with boiling water and does not show signs of reaction

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with air below 200°C. It dissolves slowly in 10^{-3} N acid and rapidly in higher than 0.1 N acid. The thermal and electrical conductivities are about the same as for graphite and large pieces of CeS heat quite well in an induction field. The molal free energy of formation at room temperature is estimated to be -120 ± 20 kilocalories.

Ce_3S_4 - It is black and has a density of 5.3. It has a cubic crystal structure and melts at 1840°C. with some slight volatility corresponding to 10^{-3} mm. to 10^{-4} mm. It can be filed and machined but is more brittle than CeS. It is a moderate electrical conductor and has a specific resistance between 10^{-2} and 10^{-1} ohm-cm. It does not react with boiling water or with air at room temperature. It is more inert than CeS toward oxidation. It dissolves slowly in 0.1 N acid. The free energy at room temperature is estimated to be 440 ± 50 kilocalories.

Ce_2S_3 - It is red with the same crystal structure as Ce_3S_4 with metal vacancies. It has a density of 5.20. It melts at 1860°C. with loss of sulfur. It is a poor electrical conductor with a specific resistance of greater than 1000 ohm-cm. The free energy is estimated to be -295 ± 30 kilocalories.

ThS - It has a silvery metallic luster with a density of 9.56. The NaCl crystal structure has a Th-S distance of 2.84A. The melting point is above 2200°C. and it has no appreciable vapor pressure at 2200°C. Its mechanical and physical properties are almost identical with those given for CeS. It dissolves slowly in cold 1-3 N HCl.

Th_2S_3 - It has a brown color with a metallic luster. The crystal structure is orthorhombic and the melting point is 1900° to 2000°C. with no appreciable volatility. It can be machined or filed readily and is

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a fairly good electrical conductor with a specific resistance of less than 10^{-2} ohm-cm.

Th_7S_{12} - It has a black color with a hexagonal crystal structure and density of 7.78. It has an electrical conductivity slightly higher than that of Ce_3S_4 and is very similar to Ce_3S_4 in its physical and mechanical properties. It melts at 1770°C. It dissolves slowly in 1 N acid.

ThS_2 - It has a purple color and a density of 7.36. It has an orthorhombic crystal structure with a Th-S distance of 2.96A. It melts at 1905°C. with loss of sulfur. It dissolves moderately fast in 1 N acid.

$Ce_{2/3}Th_{1/3}S$ and $Ce_{1/2}Th_{1/2}S$ - These solid solutions are very similar to CeS. They have a lighter brass color and dissolve somewhat more slowly in acid.

$Th_{1/2}U_{1/2}S$ and US - These are very similar to ThS in almost every respect except that they dissolve in acid somewhat more slowly.

U_2S_3 - This has a metallic gray color and is quite similar to Th_2S_3.

US_2 - This has a black color and loses sulfur at moderate temperatures.

Phases Present in Sulfide Systems.-- The phase diagrams of the sulfide systems have not been well worked out but some points can be given. There are two phases in the cerium system. The upper phase with a cubic crystal structure and the ideal formula of Ce_3S_4 has a solid solution range from Ce_3S_4 to Ce_2S_3. The lower NaCl cubic structure is believed to have a range of solid solubility from CeS to $CeS_{0.8}$. The eutectic between the Ce_3S_4 and CeS phases is at about 1700°C. The melting point

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of CeS is above 2200°C., the melting point of Ce_3S_4 is at 1840°C., and Ce_2S_3 melts at 1860°C.

In the thorium system there are four phases. ThS with a NaCl cubic structure melts above 2200°C. and apparently has no appreciable range of solid solubility. Th_2S_3 melts at 1900° to 2000°C. and has no range of solid solubility. Th_7S_{12} melts at 1770°C. and apparently has a range of solid solubility up to $ThS_{1.85}$. ThS_2 melts at 1905°C. and apparently has a range of solid solubility down to $ThS_{1.9}$. The eutectic between ThS and Th_2S_3 melts above 1800°C.

Manufacture of Sulfide Crucibles

The various materials to be used for crucibles are ground in a propane atmosphere by a ball mill until the powder passes 325 mesh. The crucibles can be made using dry powder without binder by pressing the powder into a molybdenum crucible using up to 15 tons per square inch. The crucible is then fired in the molybdenum crucible. A quicker method is to add 15 to 20 per cent by volume of naphthalene as binder. The naphthalene is added as an ether solution and the ether vaporized. The binder allows one to press in a straight cylindrical steel mold, using up to 50 tons per square inch, with a plunger shaped to match the inside of the crucible. Lauric acid is used as lubricant. The crucible is pushed out of the mold, heated at reduced pressures at 150° to 200°C. for several hours to remove the volatile material and then fired under high vacuum. The crucibles are fired for 30 minutes. Barium sulfide is fired at 1500° to 1600°C.; CeS is fired at 1750° to 1900°C. depending upon the amount of Ce_3S_4 present; Ce_3S_4 and Th_7S_{12} are fired at

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1600° to 1700°C.; ThS is fired at 1900° to 2000°C.; and Th_2S_3 is fired at 1650° to 1750°C. The uranium compounds can be fired to about the same temperatures as the corresponding thorium compounds. The crucibles shrink about 15 per cent and if the tolerance is too strict they may be machined to correct dimensions.

NITRIDE REFRACTORIES

As has been mentioned in the discussion of refractory substances and their properties, the nitrides of some of the nonvolatile metals are quite stable and have high melting points. The high tolerance for nitrogen in plutonium metal made these nitrides seem very promising as possible refractory materials, especially for the remelting operation. Considerable attention has therefore been given to the production of the nitrides of uranium, titanium, zirconium, lanthanum, cerium, thorium and tantalum, and to the fabrication of crucibles from uranium, titanium and zirconium nitrides.

Manufacture of Nitrides

Uranium Nitride.— This nitride has been prepared by the action of nitrogen and ammonia on uranium hydride, UH_3, powdered uranium and uranium shavings at both low and high temperatures. The nitrogen content of nitride prepared from UH_3 and NH_3 at 250°C. has been reported to correspond to $UN_{1.86}$. Other nitrides of uranium prepared by the above methods have been found to have a somewhat lower nitrogen content.

The higher nitrides of uranium have been found to be thermally

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unstable, nitrogen being given off. Analysis of nitride after heating under vacuum to 1700°C., or above, corresponds closely to the compound UN. This compound is apparently very stable; a nitride crucible made from this nitride has been subjected to an H_2 atmosphere at 1950 psi and 750°C. without any apparent attack on the crucible. A pressed mononitride billet was fired to 2350°C. ± 25°C. in a zirconium carbide crucible under vacuum without further decomposition, but some fusion of the zirconium carbide and uranium nitride took place at the point of contact of the two materials. The nitride did not melt at this temperature, although there were signs of incipient fusion. A sample was found to melt down completely at a temperature slightly above 2600°C.

The method used to prepare uranium nitride for crucibles is as follows: uranium nitride is prepared by passing NH_3 over clean uranium shavings at 400°C. in a stainless steel tube. The tube, 4 in. in diameter and 19 in. long, has a capacity of approximately 10 lbs. of shavings. In order to remove impurities, the NH_3 is first passed through a Pyrex tube containing uranium shavings maintained at approximately 500°C. The reaction tube is heated by means of a resistance furnace to 300°C. at which temperature reaction begins. The furnace is then shut off and the temperature continues to rise due to the heat liberated by the reaction, becoming constant at approximately 400°C. At this temperature NH_3 is introduced at the rate of approximately 3 liters per minute. When the reaction first starts, the NH_3 introduced is completely absorbed, the hydride and nitride being formed simultaneously. As the reaction proceeds, hydrogen is given off and the nitride is formed. After about 5 hours the temperature begins to drop and the furnace is again

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turned on to maintain a temperature of 400°C. and the reaction continues for another hour. Helium is then substituted for NH_3 and the temperature is raised to 700°C. and maintained at that temperature for two hours. The product when cooled to room temperature is somewhat pyrophoric, but on standing in a loosely seated container becomes passive.

Several runs have been made by the above procedure and in each case a very finely divided product was obtained. Analytical results correspond approximately to the compound $UN_{1.5}$. Sieve analysis of a typical run gave the following results: 25 per cent retained on 180 mesh screen, 35 per cent on a 325, and 15 per cent on a 400 mesh screen, with approximately 25 per cent passing a 400 mesh screen.

The nitride as produced above is not suitable for the production of crucibles. Crucibles pressed from this product and fired under vacuum to 2000° to 2100°C. were found to be badly checked and somewhat distorted. After degassing the above product under vacuum at 1650° to 1700°C., a slightly sintered product is obtained, the analysis of which corresponds fairly well to uranium mononitride. The product is not pyrophoric and can be easily handled in air at room temperature without burning. Fairly dense crucibles were prepared from this material.

It was found that in reducing the higher nitride to the mononitride by heating above 1700°C. in a graphite crucible, reaction took place between the nitride and graphite. When heating below 1700°C., analysis showed contamination by approximately 0.1 per cent carbon, while at 1900°C. approximately 0.5 per cent carbon was found in the samples.

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Titanium Nitride.— In the earlier work the titanium nitride used was from lots prepared by the hydride process under the quality designations of "regular" and "pure". The "pure" was considered by the manufacturer to be better only in the lower contamination by other metals; both grades were shown to be much lower in nitrogen than the theoretical value for TiN. Attempts to obtain a better grade of nitride have been based upon: (1) removal of impurities from commercial TiN made by the hydride process, and (2) investigation of new sources of TiN.

1. Purification of Commercial TiN. It was found possible to remove the non-opaque phases present in commercial TiN by reaction with HF. The report of the petrographic examination of one lot of the material purified in this way was: "Very clean except for rare grains of transparent material, the relatively large size of which suggests it had failed to go into solution during the purification process."

2. Manufacture of TiN from $TiCl_4$. The first procedure investigated was to introduce NH_3 into a vessel containing redistilled and purified $TiCl_4$ and to heat the resulting complex ammine to form the nitride. The procedure worked well except for the difficulty of breaking the container due to the formation of a thick crust. This was obviated by forming the complex ammine in a separate container and transferring the product to a separate vessel for removal of NH_4Cl. The analyses of some products are given in Table VI-6, where it is seen that the results are in fair agreement with the theoretical values for TiN, i.e., 77.37 per cent Ti and 22.63 per cent N.

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Table VI-6. Analysis of TiN made from $TiCl_4$

Lot No.	Titanium	Nitrogen
L-4A	76.0%	20.3%
L-4A after firing	78.5	18.5
L-6A	73.2	20.0
L-7A	77.8	21.2
L-12B	75.4	19.7

The titanium nitride made from $TiCl_4$ is satisfactory for use in the preparation of TiN crucibles without further treatment and can be supplied free of metallic impurities, limited only by the quality of the $TiCl_4$ used.

3. Manufacture of TiN from TiH_2. Since the breakage of the container used during the conversion of $TiCl_4$ to TiN presented considerable difficulty, the conversion of the hydride TiH_2 to TiN was investigated. High purity TiH_2 was procured and this was converted to the nitride by heating it to 1200°C. in a stream of NH_3. The product was entirely satisfactory from the standpoint of its analysis and had the further advantage of possessing finer particle size.

Zirconium Nitride.— The zirconium nitride prepared commercially by the hydride process was even less satisfactory than the titanium nitride. It contained only 7 to 8 per cent N, compared with the theoretical amount of 13.29 per cent, and it was not found possible to remove the oxide present by acid treatment since the material was completely soluble in dilute acids. Other sources of ZrN were investigated.

1. Manufacture of ZrN from $ZrCl_4$. Zirconium tetrachloride is

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not so easy to purify as $TiCl_4$ and the development of a successful method of making ZrN from it was much slower until a commercial source of $ZrCl_4$ of sufficient purity was found. Zirconium tetrachloride is converted to the ammine complex by means of NH_3 and this product when heated to 1000°C. forms the nitride. Analyses of several lots are given in Table VI-7. They are to be compared with 86.71 per cent Zr and 13.29 per cent N, the theoretical values for ZrN.

Table VI-7. Analysis of ZrN from $ZrCl_4$

Lot No.	Zirconium	Nitrogen
R-2B	84.6%	12.6%
R-3B	--	12.9
R-5B	--	13.1
R-7B		13.09
R-18A	87.23	13.5

2. Preparation of ZrN from ZrH_2. The conversion of ZrH_2 to the nitride is readily accomplished. In one experiment, after evacuation of the system, NH_3 was admitted and permitted to flow for 18 hours over the sample which was kept at a temperature varying between 1100° and 1200°C. Analysis of the product gave 12.93 per cent N, which is in good agreement with the theoretical value of 13.29 per cent N for pure ZrN. There seems to be no question that this procedure is a satisfactory production method for the preparation of ZrN.

Rare Earths and Other Nitrides.-- The dissociation constants of the nitrides may be used to estimate their relative stabilities and on such a basis the following have been given consideration: LaN, CeN, Misch-metal nitride, ThN_2 and TaN, all of which have high melting points,

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are stable to very high temperatures and are not too difficult to produce. In spite of their thermal stability, however, it has been found that several of them are not resistant to hydrolysis until they have been sintered and thus are somewhat more difficult to handle; those which have been shown to be definitely attacked by moisture are LaN, CeN and ThN_2. Tantalum nitride is sufficiently stable to be satisfactory; in fact, one sample of TaN which had been fired to 2000°C. in NH_3 became so resistant that it was exceedingly difficult to dissolve it for analysis. On the other hand, it has been predicted that in vacuo TaN will dissociate at 2000°C. In addition to the above stable nitrides, VN has been investigated as a possible addition agent to help in the sintering of the more refractory nitrides because of its low melting point

1. Preparation of Lanthanum Nitride. Lanthanum metal was first converted to the hydride by heating it in hydrogen at a temperature of 150° to 200°C. The hydride begins to lose hydrogen when heated above 350°C. and is completely dissociated at 1000°C. It was converted to the nitride by heating in anhydrous NH_3 to 926°C. over a period of 12 hours. Analysis of the product showed the presence of 8.96 per cent N and 88.7 per cent La, totaling 97.60 per cent. The theoretical values are 9.17 per cent N and 90.83 per cent La. Lanthanum nitride, as prepared above, is a black powder which hydrolyzes readily in the laboratory atmosphere.

2. Cerium Nitride from Cerium Metal. Cerium metal was readily converted to the hydride at 50° to 150°C. after which NH_3 was passed over the product at 975°C. for a period of 10 hours. The product contained 7.62 per cent N and 88.6 per cent Ce, to be compared with 9.1 per cent N

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and 90.9 per cent Ce, the theoretical values. The low analysis can be accounted for by the hydrolysis of the material during handling; it was found to react very readily with atmospheric moisture.

3. Thorium Nitride from Thorium Metal. A sample of compact thorium metal was heated in vacuo to 800°C. to rupture the superficial oxide film and after cooling nearly to room temperature was reacted with hydrogen. A black powder was formed about eight times the bulk of the compact metal. On reheating the hydride, evolution of hydrogen occurred above 350°C. The finely divided metal produced began to react with purified N_2 at 450°C.; absorption was very rapid at 850°C. The product was analyzed with the following results: 3.41 per cent N and 88.8 per cent Th. It appears from X-ray examination that the structure is best represented by ThN_x, where x may be 1.5 to 2. The product reacted rapidly with atmospheric moisture which may account in part for the low analysis.

4. Preparation of ThN_2 from $ThCl_4 \cdot 8H_2O$. It has been shown possible to dehydrate $ThCl_4 \cdot 8H_2O$ by mixing it with NH_4Cl and heating up to 320°C. in a stream of dry, gaseous HCl. When the residual $ThCl_4$-NH_4Cl mixture is heated in NH_3, NH_4Cl is evolved and at 1000°C. a product is obtained which contains nitrogen in amount corresponding nearly to the theoretical for Th_3N_4 but in addition an atom of chlorine. When this white material is heated for an hour at 1600°C. in NH_3, it is converted to a yellow nitride. Analysis of one sample showed the absence of Cl and the presence of 4.3 per cent N. The nitride hydrolyzed rapidly in the laboratory atmosphere.

5. Tantalum Nitride. A lot of TaN which had been prepared from metallic Ta contained 6.88 per cent N and 92.0 per cent Ta, a total of

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98.88 per cent. The theoretical analysis for TaN is 7.2 per cent N and 92.8 per cent Ta. This material was quite superior to that prepared from the oxide.

6. Vanadium Nitride. Ammonium meta vanadate when heated in an atmosphere of NH_3 decomposes to yield an impure vanadium nitride. Two lots analyzed 11.2 per cent N and 74.4 per cent V; and 9.0 per cent N and 71.9 per cent V, respectively. From an X-ray examination it was estimated that the sample contained 80 per cent VN.

Manufacture of Nitride Crucibles

Uranium Nitride.-- Crucibles of this nitride have been prepared by several means but the best results have been obtained by pressing the powdered nitride in a die to give a crucible of the desired shape, followed by the usual vacuum firing to above 2000°C. Particle size was found to be an important factor. It was practically impossible to form a crucible by either tamping or pressing with a particle size greater than 325 mesh. A mixture containing 60 per cent +325 mesh and 40 per cent -325 mesh was found to press fairly well.

Nitride crucibles prepared by tamping and sintering in a graphite form were found to be very porous with the surfaces in contact with the graphite considerably contaminated with carbide and, in general, very unsatisfactory.

Crucibles were prepared by pressing a mixture of powdered uranium metal with the higher nitride in the proper proportion to give the mononitride and firing these crucibles to different temperatures. The resulting crucibles were not as well sintered and were more porous than

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crucibles pressed from the mononitride and fired under identical conditions. The metal and nitride mixture could be easily pressed into crucible form but the bulk density before firing was much less than that for the mononitride.

Small crucibles can be pressed from the mononitride powder without much difficulty but large crucibles cannot be pressed from the dry powder due to the poor transmission of pressure between the nitride particles and also due to the weak bond between the particles after pressing. Pressures were used in the range from 50,000 to 180,000 psi. Paraffin has proved satisfactory in improving the transmission of pressure as well as acting as a bond between the particles to facilitate handling prior to firing. Approximately 0.5 to 1.0 per cent by weight of wax dissolved in CCl_4 has been used with satisfactory results. The paraffin wax distills off during the initial firing.

Analyses of sintered nitride crucibles have been reported as follows:

Per cent U	Per cent N	Per cent C
93.8	4.15	0.43
93.6	4.08	0.44
93.5	4.10	0.47
94.5	4.10	0.52
93.6	3.30	0.51
92.4	4.27	0.58

All the above crucibles were heated to 2000° to 2100°C. under vacuum in a graphite container with only the bottom of the crucible in contact with the graphite.

Titanium Nitride.— The following methods of producing TiN crucibles have been used: dry pressing and slip casting. When it was found that a simple dry pressing technique resulted in a very porous crucible, attention was turned to the development of slip casting techniques. A suitable

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slip was formulated and with it, it was possible to produce crucibles with higher density and smoother inner surfaces. A return to dry pressing methods was made to determine whether it was possible to improve the articles by admixtures of other nitrides and sulfides to aid in sintering. The results of these studies will be given below.

During the investigation considerable information has been obtained on the influence of the furnace atmosphere. In the early experiments, all firing was done in vacuo, but due to the thermal instability of TiN above 2000°C., material was lost from the surface and the crucibles produced had a sandpaper-like texture; at 2100°C. in one instance, so much of the crucible material was lost that a hole was "burned" through one side. Analyses of the crucibles fired in vacuo showed very little change in composition. Use of an inert gas, helium at atmospheric pressure, for example, gave a crucible with an improved appearance. Dissociation of the TiN on the surface was inhibited and the crucibles showed smaller loss of material. The best atmosphere in which to fire nitride crucibles, however, proved to be one of ammonia. The dissociation and loss of TiN is repressed and, in addition, any residual TiO_2 in the nitride is converted to nitride. Also, if carbon is present, either free or as carbide, it is removed and the crucible is converted more or less completely to nitride. The color of the crucibles is greatly improved and the smooth surface of the original slip cast or pressed article is retained. An analysis of a fired crucible gave the theoretical amount of Ti but was low for N, probably due to the method used in dissolving the sample.

The apparent porosity and density of the crucibles were determined

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by weighing them in air, immersed in pentachloroethane and suspended again in air together with the absorbed immersion liquid. These data, together with measurements of the shrinkage, give a picture of the characteristics of the crucible as a whole. To determine the porosity of the inner surface the crucible was immersed in a fluorescent dye solution and after removing the excess the surface was examined in ultraviolet light. This method is an adaptation of the dye absorption test used on white ware which is required because of the highly colored metallic surfaces of nitride ware.

1. Dry Pressed Type N Crucibles of TiN. Tamped crucibles, prepared from finely divided TiN, were not satisfactory, so the formation of crucibles under pressure was investigated. Small laboratory hydraulic presses and screw presses are satisfactory, but for obtaining maximum compression the use of a large hydraulic press is required. Even with the proper distribution of particle sizes, however, it is not possible to produce non-porous crucibles by simple dry pressing methods. For example, crucibles prepared in steel molds from both purified TiN and TiN synthesized from $TiCl_4$, and fired both in vacuo and in ammonia at 2000°C., possessed on the average a porosity in the neighborhood of 40 per cent and a specific gravity of 3.2. The density given in the literature for TiN is 5.17 grams per milliliter. The crucibles had a good appearance and were hard enough to scratch glass.

Good crucibles of much lower porosity were obtained, however, by the addition of 10 per cent "Carbowax 4000" as a mold lubricant. All of the TiN was fine enough to pass a 325 mesh sieve and 33 per cent was below

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10 microns. The crucibles possessed a golden yellow metallic luster, were hard and nearly non-porous.

2. Slip Cast Type C Crucibles of TiN. It was found possible to slip cast TiN from an aqueous suspension in plaster of Paris molds. A satisfactory slip was prepared by grinding 200 grams of TiN (purified) with 180 cc. H_2O and 1920 grams of one-half inch steel balls in a one-quart mill for 28 hours. Grinding for 48 hours resulted in crucibles which cracked on drying, due to too low particle size. The iron was removed by HCl and the product washed with water until free from chloride ions. The slip was made up to a specific gravity between 1.5 and 1.6, was deaerated and poured. It could not be used after standing for 24 hours.

Type C crucibles, prepared from the TiN slip, were fired in ammonia up to 1500°C. in a "Zircofrax" tube heated in a "Globar" furnace. By prefiring slowly to this temperature the crucible became sufficiently well matured to withstand the rapid rise in temperature experienced in the high firing operation. They were then high fired in ammonia in a molybdenum cylinder heated by induction. One such crucible showed a specific gravity of 4.8. The inner surface possessed a satin-like surface with a fine yellow metallic luster and the crucibles were strong and hard.

3. Effect of Admixtures to TiN. Since satisfactorily non-porous crucibles could not be produced by a simple dry pressing technique, the effects of adding other materials to TiN were investigated. Some of the materials were added with the idea that interaction with oxides present in the TiN would remove the latter as volatile compounds.

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Carbides such as tungsten carbide, WC and uranium carbide (UC) had the effect of removing any tendency toward shrinking, and the crucibles produced had very high porosity, 50 per cent, and very low specific gravities, 2.9. They were sufficiently well bonded, however, to be mechanically strong and hard enough to scratch glass.

The effect of adding other nitrides, for example, uranium nitride, vanadium nitride and tantalum nitride were also investigated. The results are somewhat ambiguous since all of the added nitrides contained large percentages of oxides and, in some instances where an NH_3 atmosphere was used, these were converted in part to the nitride, at least superficially. Only one experiment was carried out with uranium nitride, and the result showed little interest. Except for one crucible, vanadium nitride up to 10 per cent, seemed to inhibit shrinking; when this particular crucible was fired in NH_3 at 2100°C. for 20 minutes, on the other hand, fusion occurred. The lump produced had higher density and low porosity, and X-ray examination showed the presence of a (Ti,V)N solid solution phase. The addition of impure TaN had a very favorable effect and produced crucibles of excellent appearance. As the percentage of TaN was increased, the shrinkage increased and the porosity decreased to a very low value. The best results were obtained by firing a 50 per cent mixture at a temperature over 2000°C. for a short time. With these well sintered products the shrinkage at the top was much greater than at the bottom and the crucible had the shape of a milk bottle. This is related to inequalities in pressure during the molding and can only be corrected by use of molding lubricants.

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The effect of adding pure cerium sesquisulfide, Ce_2S_3, was also very encouraging. With 50 per cent admixtures, fired in NH_3 at 1800° to 1900°C. for 20 minutes, very dense crucibles of low porosity were obtained. Again, the large variation in the shrinkage from top to bottom is to be accounted for by poor flow during the formation of the crucible.

4. Attempt to Hot Press Nitride Crucibles. Attempts to form crucibles by compressing nitrides in graphite molds at temperatures around 2500°C. were not successful. The method used was that developed by an industrial company and experiments carried out in their plant as well as in the laboratory led to the formation of carbide. There was so little hope that the method might be utilized, the work was dropped.

Zirconium Nitride.-- The remarks made concerning TiN crucibles also apply to the production of zirconium nitride crucibles. Most of the attention was given to TiN since the supply of good material was more plentiful, but no differences in methods are anticipated for ZrN.

HIGH MELTING POINT METALS

Molybdenum.-- This is the most practical refractory metal for most purposes at temperatures up to 2200°C. because it is readily available and can be worked without too much difficulty, and because of its inertness.

Molybdenum cylinders and crucible containers are most conveniently

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made from sheet by cutting out a circular bottom for the crucible and rolling sheet into the shape of a cylinder. The cylinder and bottom are then welded together on a graphite form by atomic hydrogen welding. The walls can be made of any thickness from 0.005 to 0.010 inch up to 0.06 inch. It is rather difficult to roll sheet thicker than 0.06 inch into cylinders smaller than two inches in diameter. Cylinders and crucibles can also be made by drilling out Mo rods. The surfaces can be machined to give smooth polished surfaces and the walls can be made as thin as 0.030 inch. When the desired object must be of exact dimensions, this is the most suitable method. Powder metallurgy techniques can also be used to make Mo objects, but this method is by necessity confined to thick-walled objects and would be used ordinarily only for objects larger than one inch in diameter for which Mo rods would not be available.

The Mo cylinders with or without bottoms make very excellent heating elements for induction heating. If the diameter of the cylinder is decreased below 15 mm. (0.625 inch), the heat generated in a 30 kilocycle induction field falls off rapidly. For the most efficient use of the induction field, the wall thickness of the cylinder should be at least 1.5 mm. (0.06 inch) if there is no conducting material inside the cylinder.

Aside from using Mo for crucibles and heating elements, it has a very important use as radiation shields. The only type of radiation shield that need be given special notice is the very thin shield used in the case of induction heating. The cylindrical radiation shields used for the sides opposite the heating element must be very thin so that the shields

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will not take any large amount of energy from the induction field. For this purpose, 0.002 inch Mo foil is used. It may be used in the form of cylinders or as spirals with the turns kept slightly separated. The ends may be spot-welded or riveted together. These shields are extremely effective insulators at high temperatures and are advantageous in that they do not give off gas after having been once used.

The behavior of Mo at high temperatures either in vacuum or inert gases is very satisfactory. It is not susceptible to hydrogen as are some metals which become very brittle and crack. Molybdenum which has been heated above 1500°C. is considerably more brittle than ordinary commercial Mo because of recrystallization, and it cannot be worked after having been heated to high temperatures; however, it can be handled quite easily without much trouble due to cracking. Molybdenum is not attacked by oxygen-containing gases in the presence of H_2. In the absence of H_2 it is attacked by water or oxygen to form black MoO_2 as a coating. Above 1200° to 1400°C., MoO_2 disproportionates and only the volatile MoO_3 is formed, leaving a clean metal surface. This allows ready cleaning of the metal surface by vacuum heating. If the oxygen concentration is low enough to prevent vaporization through formation of MoO_3, molybdenum is quite nonvolatile up to 2200°C. In a vacuum at 2200°C., Mo will lose 22 mg. per sq. cm. of surface per hour or it will evaporate at the rate of 0.02 mm. thickness per hour which is excessive for the thicknesses commonly used. Also, above 2200°C., Mo becomes soft enough to lose its shape under moderate pressure. Therefore, although Mo is the most practical refractory metal up to 2200°C.,

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it is not very useful above 2200°C. and must be replaced by W, Re or Ta.

Rhenium.-- Although Re is a very rare element and has had little use as a refractory metal, its properties indicate that it should have some very distinctive uses. It is very high melting and nonvolatile and, in fact, available data indicates that it is almost as refractory as tungsten. The greatest promise of Re lies in its nobility. Its oxides, sulfides, halides, nitrides and other common compounds are all much less stable than the corresponding compounds of Ta, Mo and W. Therefore, it should have much less tendency to reduce compounds compared to Ta, Mo and W. This is of considerable advantage not only in the use of the metal as a container for preparative purposes but especially in the determination of vapor pressures. Ta, for example, is usually not well suited as a container for compounds in an apparatus for the determination of vapor pressures because it readily reduces most compounds to give a volatile Ta compound. This type of reaction often invalidates the results of the vapor pressure experiment and might be avoided by the use of Re.

Tungsten.-- This is the most refractory of the readily available metals and is a suitable crucible material for metals in which it is not too soluble. Satisfactory crucibles may be obtained commercially which are formed by pressing the powder to shape and sintering in hydrogen. Such crucibles are capable of holding molten uranium for periods of six hours or longer at temperatures up to 1400°C. The

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The solubility of tungsten in molten uranium has been found to be as follows:

Temperature, °C	1200	1300	1400
Solubility, per cent	0.54	0.88	1.14

Tantalum.— Due to its high melting point (ca. 2850°C.), low volatility, and resistance to attack by many chemical reagents, this metal has been tried as a container material for remelting plutonium. It is sufficiently ductile and malleable to be formed into crucibles without difficulty. Unfortunately, plutonium wets tantalum so strongly that in most cases it cannot be peeled off of the plutonium ingot completely. This difficulty is encountered even when the remelting temperature is held to 850°C. or below. For the above reason, tantalum is no longer of interest as a refractory for reduction or remelting operations.

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